ELECTRONIC STRUCTURE OF METAL ION-DIOXYGEN COMPLEXES

Thesis by

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"The time has come, the walrus said, to talk of many things."

- Lewis Carroll

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ABSTRACT

The electronic structures of cobalt complexes containing O_2 units as ligands have been investigated, primarily by electronic spectroscopy. Various cobalt complexes containing the structural units present in the O_2 complexes were investigated, and a systematic and self-consistent classification of their ligand field electronic transitions, charge-transfer electronic transitions, and excited state reactivities developed, which provided a basis for understanding the O_2 complexes.

The O_2 complexes investigated were all found to contain low-spin d^6 cobalt(III) central metal ions, by spectroscopic criteria, and either peroxide or superoxide ligands. The O_2^{n-} ligands have positions in the spectrochemical series between those of ammonia and water, and have characteristic charge-transfer transitions in their complexes, superoxide complexes showing low energy metal-to-ligand transitions, while both superoxide and peroxide complexes show characteristic ligand-to-metal transitions in the UV. Extensive comparisons were made to O_2 complexes of other metal ions, and the binding of dioxygen to metal ions concluded to be oxidative addition in general. Autoxidation of metal ions and the structures and properties of oxymetalloproteins have been considered in the light of these results, and the formulation of addition of O_2 to Cu(I) and Fe(II) as one- and two-electron oxidative addition, respectively, is discussed.

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CHAPTER I

Bonding Interactions of Dioxygen

Introduction

Biological oxygen metabolism is fundamentally related to the interaction of the dioxygen molecule (O_2) with metal ions. Such interaction is most directly reflected in the reversible formation of complexes involved in oxygen storage and transport, but chemical reduction of dioxygen, yielding energy and/or organic substrate modification, also generally involves the transitory formation of metal ion-dioxygen complexes. Despite the obvious importance of the nature of the bonding in such complexes, our current understanding of their electronic structure can at best be described as being extremely primitive, the most important reason for this being that in not a single case do we know the geometry of the metal-dioxygen bond in a dioxygen-metalloprotein complex. Crystal structures are known for only two oxymetalloproteins, the extremely similar molecules oxyhemoglobin and oxyhemoglobin,[11] and in these two cases the dioxygen molecule has not been directly detected, although we at least now know the geometry of the binding sites. Furthermore, no isolable model "small molecule" dioxygen-metal ion complexes have yet been reported for the biologically important metals, iron and copper.

However, a rather large number of stable dioxygen complexes are known with other metal ions, cobalt and iridium,

for example. The small size of these molecules has allowed accurate structural determinations, and a variety of geometries for the M-O_2 linkage are known for various compounds. Unfortunately, it seems quite clear that none of these can be naively accepted as models for either the geometry or the electronic structure of the metal-dioxygen bond in the biological systems, if for no other reason than that the d electron configurations of the metal ions in these complexes are different from those in the metalloproteins.

Detailed analysis of the electronic properties of these complexes should nontheless give, at least in principle, considerable information concerning the various factors involved in the bonding of dioxygen to metal ions. We should hope to gain understanding by such study of the energies and spatial properties of the O_2 orbitals important in bond formation, the subtleties of their interaction with metal ion orbitals, and the detailed dependence of such interaction on the oxidation state, d electron configuration, etc., of the metal ion. Our ability to correlate the properties of various complexes, and, further, to extrapolate to rather different situations where we have much less information, such as the metalloproteins, is largely dependent on our ability to separate these factors.

Dioxygen is an unusual ligand by the standards of inorganic chemistry, in many respects. Its half-filled π^* orbital provides for unusual possible donor and acceptor bonding interactions, and also produces an exceptional potential for electron transfer from

metal ions, the anions O_2^- and O_2^{2-} being rather stable chemical species. In fact, as we shall see, there is no established example of a metal ion-dioxygen complex which does not have a ground state characterized by such electron transfer. This situation presents us with considerable possible ambiguity in the electronic description of the ground states, and forces us to consider the problem of defining oxidation states metal ion complexes.

Oxidation and Oxidative Addition

The concept of oxidation-reduction, the transfer of electrons between two definite chemical species, is a pervasive and thoroughly accepted one in chemistry. We wish to consider the rather special case of oxidative-reduction with simultaneous formation of a chemical bond. The best examples of such a reaction occur in transition metal chemistry. Consider, for example, the reaction:

(1) $$Co(CN)_5^{3-} + Br\cdot \rightarrow Co(CN)_5Br^{3-}$$

We formulate the product as the six-coordinate (distorted octahedral) complex of low-spin d^6 Co(III) with five cyanides and one bromide ligand. The reason for the retention of the bromide anion in the coordination sphere, rather than release as free bromide, is the well-known strong energetic preference of low-spin d^6 systems for octahedral coordination, whereas low-spin d^7 Co(II) shows a preference (rather much less marked) for 5-coordination. (Co(III) complexes are kinetically inert for related reasons.) Such a reaction (oxidative addition) requires a reactant metal complex which is electron-rich and coordinatively unsaturated (relative to

the product metal complex.) That an oxidation reaction has indeed occurred is strongly indicated by the steric and kinetic properties of the product, as well as by the more fundamental indication of electronic structure given by the electronic spectroscopy of the complex, which is quite definitely that of a Co(III) complex (vide infra). (That the exchange reactions of the product in aqueous solution involve substitution of bromide can also be taken as support for such partitioning of the electrons in the complex, but this is a highly fallible type of argument. The whole is not equal to the sum of the parts, etc.)

The above reaction can, in many respects, be considered as the reaction of two free radicals, their unpaired electrons coupling to form a filled molecular orbital which could conceivably have been composed equally of ligand and metal character, in which case we could only have spoken of a covalent bond. In the actual case, the resultant molecular orbital is overwhelmingly ligand in character, and we can talk in terms of a bromide complex of Co(III).

"Stable" free radicals are rather uncommon, either as reactants or complexed products, and the above type of reaction is not a very general one. (In the laboratory, this reaction would be done employing Br_2 as a reactant, with resultant complications in the mechanism.)

A much more well studied reaction is that of the type[2]

(2) $$ML_n + XY \rightleftharpoons ML_n(X)(Y)$$

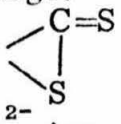
to which the term oxidative is, in fact, normally reserved. Here, the central metal ion has both its oxidation state and coordination increased by two units. Again, the complex ML_n is required to be electron-rich and coordinatively unsaturated. The best examples of such reactions are those of complexes of metals with a d^8 configuration, notably the kinetically inert, low-spin, square planar complexes of Rh(I) and Ir(I), the products then being octahedral complexes of low-spin d^6 Rh(III) and Ir(III). Some transition metal complexes of d^{10} configuration also exhibit such reactions, the products then being low-spin d^8 square planar complexes. These later reactions, however, have more complicated mechanisms which usually involve expulsion of a ligand, the d^{10} complexes not having a very strong preference for any single coordination number but generally having more than two ligands. In any case, an important feature of the reaction is that neither the reactants nor products need be "free radicals", and, for related reasons, the reactions are often completely reversible.

An interesting example is the reversible formation of cis-dihydrides by reaction of a d^8 complex with molecular hydrogen,

(3) $$ML_4 + H_2 \rightleftharpoons \text{cis-}ML_4H_2$$

A plausible micro-mechanism for this reaction involves passage through a "5-coordinate" d^8 complex in which a bond is formed by donation from the metal into the vacant H_2 σ^* antibonding orbital, leading to, in the limit, a coordinated H_2^{2-} ion. Little or no bonding character would remain in the H-H bond, and the product would be formulated as a cis-dihydride. Such a concerted mechanism is

strongly indicated by the necessity to avoid involvement of H-H bond scission in the activation energy for the reaction, the energy of the H-H bond in free H_2 being greater than 100 kcal-mol^{-1}.

Molecules that contain multiple bonds can add oxidatively without cleavage to form complexes with 3-membered rings. Carbon disulfide, for example, forms products with a M  unit.[3] We formulate the product as a complex of the CS_2^{2-} ion, two electrons having been inserted into a π^* antibonding orbital, leading to loss of a π-bond in the ligand. The geometry of the product is, of course, consistent with this hypothesis.

Many other molecules show analogous oxidative addition reactions, alkynes providing some particularly interesting examples. Diphenylacetylene reacts with the triphenylphosphine complex of Pt(O), $Pt(P\phi_3)_4$, to give an adduct $(\phi_3P)_2Pt(\phi\text{-}C_2\text{-}\phi)$, which X-ray crystallography shows[4] to have an alkyne ligand best considered to be a bidentate, divalent ligand, the PtP_2C_2 unit being planar and the C-C bond distance (as well as the ν(C-C) in the infrared) being greatly reduced from those in the free alkyne. Acetylene reacts with $Co(CN)_5^{3-}$ to give a complex $(Co(CN)_5)_2C_2H_2^{6-}$ with a trans-μ-ethyleno unit bridging two pentacyanocobaltate units, and we again infer that two electrons have been inserted into an acetylene π^* orbital. (This reaction incidentally provides an example of the common course of reactions of 2-electron oxidant ligands with metal ions which are only 1-electron reductants, the "complexed free radical" ligand presumably produced upon reaction with one metal ion further reacting with another metal ion to form a bridged dimer, or two monomers in the case of a non-multiply-bonded ligand.)

However, alkynes also form complexes such as[6] trans-$PtCl_2$(p-CH_3-C_6H_4-NH_2)(t-Bu-C_2-t-Bu), where the alkyne fills only one coordination position of a square planar d^8 complex, the C_2 unit being orientated perpendicular to the plane defined by the $PtCl_2N$ unit. The rather short C-C bond distance, as well as the geometry of the complex, seem to strongly indicate that the ligand is here best described as a neutral alkyne, interacting in a π-acceptor fashion with d^8 metal orbitals. (Infrared spectroscopy supports a differentiation of the alkyne ligands in the two kinds of complexes, the "π-bound" alkynes having C-C stretching frequencies close to those of the free alkynes.)

Olefins provide the best known examples of such bonding. The anion of Zeise's salt,[7] $PtCl_3(C_2H_4)^-$, has been known for 140 years, and has an ethylene molecule bound in a fashion similar to that of the alkyne in the previous complex, with a C-C bond distance entirely indicative of a complexed olefin, rather than a "metallocyclopropane."

Further confusing the issue, Ir(I) and Rh(I) complexes form weak adducts with olefins[2] which are probably best described as 5-coordinate d^8 complexes, analogous to the carbon monoxide adducts.[2] However, olefins substituted with strongly electron withdrawing groups, such as C_2F_4[2] and $C_2(CN)_4$,[7] form adducts in which the C-C bond distance is quite long, and oxidative addition seems indicated. Particularly in the case of these complexes,

geometrical considerations are ambiguous indicators of electronic structure (and are clearly rather indirect and fallible in general).

Free $C_2(CN)_4$ is obviously rather different from free C_2H_4, and shows a stable monoanion and dianion in solution,[8,9] the electron withdrawing substituents decreasing the energy of the π^* orbital. (Similarly, the π^* orbitals are at lower energy in alkynes than in olefins, that is, alkynes are more oxidizing than olefins, accounting for the relatively greater preponderance of oxidative addition reactions for the alkynes). Our problem is that a continuous gradient is clearly possible between the extreme cases M-L and M^{2+}-L^{2-}, all a matter of how we lable the highest filled orbital in the complex. (A possible situation M^{1+}-L^{1-} might even be suggested by the stability of $C_2(CN)_4^-$.) The concept of partial oxidation states, correlated with reversibility of reactions, has been suggested for iridium complexes,[2] and this idea is certainly realistic in many respects. However, such a concept has rather little connection to the concept of spectroscopic oxidation states.

Well-Defined Oxidation States

The gaseous monatomic ions show line spectra involving transitions to many excited states and it has long been known that the spectra could be very adequately explained by invoking transitions from a ground state having a well-defined electron configuration to various higher J levels. Indeed, all of the J-levels predicted for a given configuration have often been identified. It might be emphasized that this is observed in spite of the fact that the ground

states of many-electron systems are undoubtedly not well described by single Slater determinants.

It was only natural that an attempt should be made to extend the theoretical machinery developed for the gaseous ions to the stable complexes of metal ions. Needless to say, the attempt was successful, and the vast majority of transition metal complexes have electronic spectra which fit the ubiquitous Tanabe-Sugano diagrams[10] extremely well. These are simply diagrams of the energies of the states arising from a given d electron configuration in a cubic field as a function of a single (fundamentally empirical) splitting parameter, Δ. (The electron repulsion (Racah) parameters B and C, which define the limit as $\Delta \rightarrow 0$, are also taken as empirical parameters, as they are generally reduced from their values in the free ions. Consideration of lower symmetries than cubic requires the introduction of additional splitting parameters.)

Octahedral high-spin d^5 Mn(II), for example, has an extremely complicated characteristic d-d spectrum in its complexes showing far more transitions than the number of parameters in the Tanabe-Sugano diagram, and its spectrum can be fit quite well. Even in cases where a very large number of transitions is not observed, such as octahedral low-spin d^6 Co(III) complexes (for which, at best, four transitions are observed), the ligand field spectra can be fit well, for "reasonable" parameter values, for complexes such as $Co(NH_3)_6^{3+}$ (for which a specification of the oxidation state of the central metal as (III) should surprise or

offend no one.) Furthermore, substitution of the ligands of such a complex changes the energies of ligand field transitions in predictable ways as a function of symmetry and ligand, and the establishment of such correlations between different complexes provides a further measure of internal consistency. It can thus be stated that, in a rather fundamental way, most transition metal complexes have well-defined spectroscopic oxidation states.

The concept of the transferability of ligand properties is closely related to the above. A spectrochemical series is a compilation of the ligand field splitting parameter Δ as a function of ligands for a given metal ion, and we can correlate the importance of various types of bonding interactions for a given ligand with its position in a spectrochemical series. The series is observed to be relatively invariant from metal ion to metal ion, and the inevitable rule-proving exceptions can at least be rationalized by reference to differences in oxidation state and other such factors.

Finally, the energies of charge-transfer transitions (which formally involve electronic transitions between pure ligand and pure metal orbitals) can similarly be correlated with the oxidation states and d configurations of central metal ions, and can provide independent evidence for a given spectroscopic oxidation state in favorable cases. All such spectroscopic correlations are, of course, highly dependent upon the existence of a well-defined spectroscopic oxidation state for the central metal ion, providing a constant base against which to measure other effects.

Such correlations are observed in spite of the fact that we know covalent bonding with ligands is important in transition metal complexes, and that the characteristic splitting parameters of ligand field spectra are due to such interactions. The observation of abnormally large intensities for bands assignable as d-d transitions, and values of the Racah parameters which are extremely decreased from the free-ion values, is particularly symptomatic of such "covalency!" Nevertheless, many examples are known of spectra of transition metal complexes which show these effects yet fit pure ligand field assignments extraordinarily well energetically.[68] (It is tempting to suggest that, in such cases, where the transitions may well be between one-electron levels having very considerable ligand character, the energetic relationships of d-d transitions continue to hold true because the transitions still involve a transfer of, roughly speaking, a single d electron from one level to another, and the relative energies of the ground state and excited states have the same relationship as if the transition were one between pure d levels. This argument approaches the level of arguments over the number of pins that can be stuck in an angel, however. The key point is that the spectroscopic oxidation state remains well-defined.)

Of course, examples do exist of complexes which probably have very poorly defined oxidation states, particularly those of certain sulfur ligands,[12] which show redox properties which seem indicative of very strong ligand-metal orbital mixing. (It is a perhaps

necessary, although not sufficient, aspect of such complexes that known examples all have complex low-energy charge-transfer spectra, and "ligand-field" transitions are not obvious, if, indeed, they exist.

We will consider the case of a ligand X_2 (acetylene, for example) having a low-lying empty π^* orbital, coordinating to a d^8 metal complex. The correlations between the d orbitals of a square planar complex and those of a product cis-octahedral complex are quite complicated, so we will consider the reactant d^8 complex to be already in such a geometrical configuration (that is, cis-octahedral with vacuum for two of the ligands). The highest filled orbital in such a complex is a σ-antibonding orbital directed towards the empty coordination positions, which we might, somewhat inexactly, call the $d_{x^2-y^2}$ orbital. Upon interaction with an empty π^* orbital on X_2, bonding and antibonding orbitals are formed. In figure I-1, we show crude molecular orbital diagrams of such interaction. In Case I, we assume the π^* orbital is relatively high in energy, and interaction is small, the bonding (filled) orbital being primarily metal in character. The complex would be well described as a distorted octahedral complex of low-spin d^8 configuration. (In an actual case, of course, the complex would probably be much closer to "5-coordinate," as the interaction with X_2 would probably not be strong enough to force the ligands of the reactant complex very far from co-planarity.)

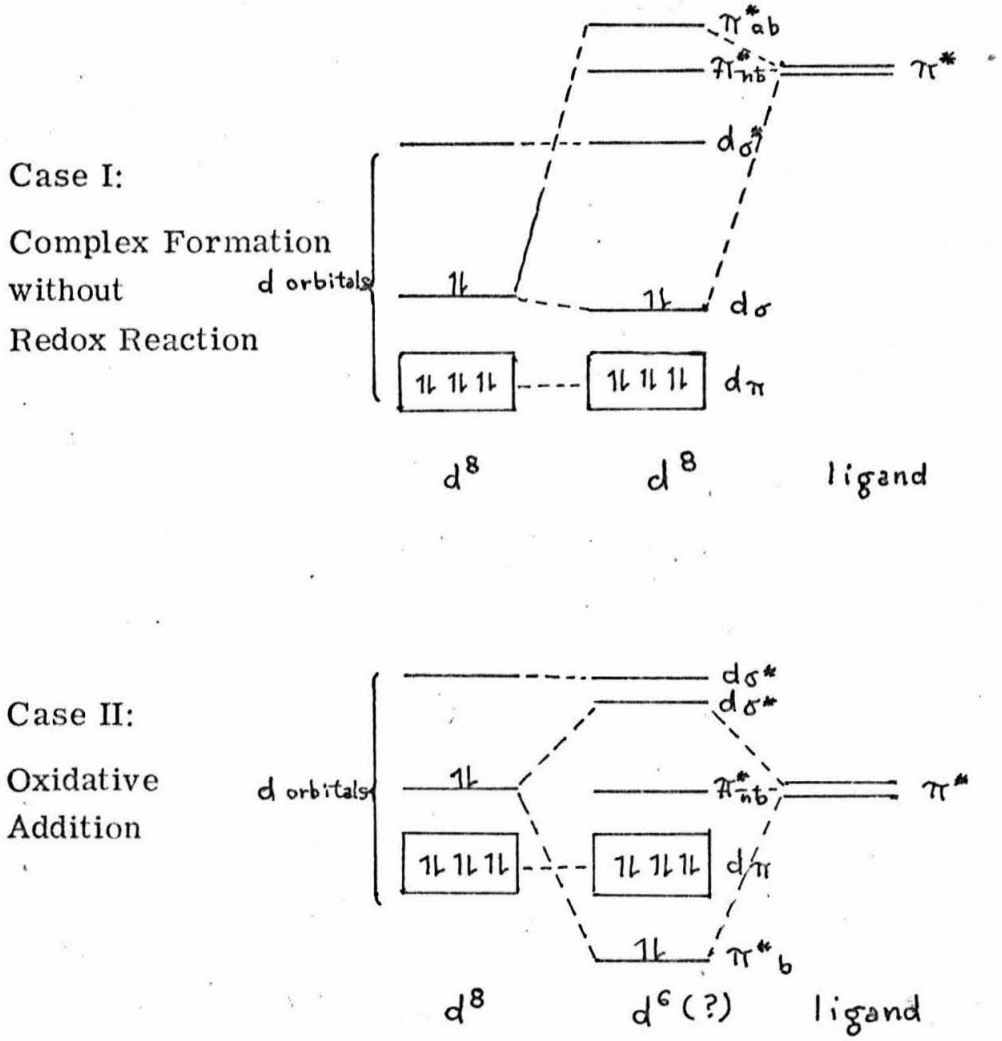


Figure I-1. Molecular orbital diagrams for interaction of a d^8 complex with a ligand X_2 having a low-lying empty π^* orbital. (See text.)

In Case II, we show an example of oxidative addition, with an empty π^* orbital at an energy comparable to that of the highest occupied metal orbital. (Factors other than one-electron energies are also important, but we are neglecting this point for our present purposes.) We have, quite purposefully, chosen a case in which metal-ligand mixing should be considerable. Decreasing the energy of the empty π^* orbital ad absurdum would result in a situation where interaction would simply result in the highest d electrons dropping down into the π^* orbital (producing, assuming that two $d\pi$ electrons did not also drop down, a d^6 cis-octahedral complex with, effectively, vacuum in the cis-positions, and a large splitting between the two $d\sigma^*$ orbitals.) In the situation we have drawn, the complex is a d^6 complex to the extent that transitions to the two levels that we have labeled $d\sigma^*$ from the $d\pi$ levels can be identified as ligand field transitions. If we had drawn the diagram from the alternative starting point of a d^6 complex plus X_2^{2-}, the splitting of the $d\sigma^*$ would then obviously represent the difference in bonding characteristics of X_2^{2-} and the other ligands of the complex, the $d\sigma^*$ orbitals being degenerate in full octahedral symmetry. Deviations of these transitions from a distorted octahedral pattern, either in terms of energies ("strong distortions") or intensities ("charge-transfer mixing") would be symptomatic of a poorly-defined oxidation state.

Our definition of oxidation states is not at all equivalent to specifying orbital populations, etc. It simply depends on a

"satisfactory" classification of the manifold of transitions between the ground state and the lowest excited states of a metal complex. (It is probably not possible to overestimate the importance of group theoretical considerations to the general applicability of the concept.) Given a well-defined spectroscopic oxidation state, we can describe the electronic properties of a complex and separate out the bonding interactions of a given ligand, and our ability to do this is, to a large extent, independent of orbital mixing.

Dioxygen and Its Anions

The dioxygen molecule was historically important in the development of molecular orbital theory, having a triplet ground state, $^3\Sigma_g^-$, corresponding to the configuration $\pi_u^4\pi_g^2$. In the gas phase, it has a variety of spectroscopically observable excited states of which we will mention the states[13] $^1\Sigma_u^-$ (32.7 kK), $^3\Delta_u$ (34.3 kK), and $^3\Sigma_u^+$ (35.0 kK), which are the lowest excited states corresponding to the $\pi_u^3\pi_g^3$ configuration. (The vibrational frequencies of these states are ~ 800 cm^{-1}, decreased from 1580.4 cm^{-1} in the ground state, and correspond fairly well to an O_2 single bond as in hydrogen peroxide.) For comparison, the O_2^- (superoxide) ion,[15] either in solution in acetonitrile or as the solid potassium or sodium salts (by reflectance or dispersed in KCl) shows its lowest energy transition at ~ 41 kK, the assignment presumably being to a somewhat perturbed $^2\pi_g \rightarrow {}^2\pi_u$ ($\pi_u^4\pi_g^3 \rightarrow \pi_u^3\pi_g^4$) free ion transition. The first four ionization energies of O_2, measured by photoelectron

spectroscopy, are[14] 101 kK($1\pi_g$), 135 kK ($1\pi_u$), and 145 kK and 162 kK ($^4\Sigma$ and $^2\Sigma$ states from $2\sigma_g$), and give somewhat more direct information on the electronic structure of O_2, the interpretation of the energies of the molecular excited states being somewhat complicated.

Carbon monoxide, which interacts with metal ions via a synergistic mechanism[16] involving σ-donation from its 3σ orbital and π-acceptance into its vacant 2π ("π_g") orbital, has the ionization energies[14] 113 kK (3σ) and 134 kK (1π). These data suggest that the only O_2 orbital which is important in its interactions with metal ions is the $1\pi_g$ (π^*) orbital. A faint possibility could exist for π-donor interactions involving the $1\pi_u$ orbital, but the unimportance of such interaction in the CO complexes, where the analogous orbital is of similar energy, as well as the unimportance of such interactions in the isoelectronic dinitrogen complexes,[17] where σ-donor bonding is weakened, strongly suggests that $1\pi_u$-metal interaction would be weak. The $2\sigma_g$ orbital seems to be <u>much</u> too low energy to be important in bonding interactions.

This brings up an interesting point. It is quite common to describe the bonding in small molecule complexes in terms of sigma-bonding from sp or sp^2 hybrid orbitals. The concept of hybrid orbitals is clearly a useful one for carbon compounds, but we note that the s-p separation in atomic oxygen is nearly 120 kK,[11] three times that of carbon, and hybridization begins to seem to be

a rather poor approximation for oxygen compounds. As implied by the data already presented, the formally bonding $\sigma 2p$ orbital in triply-bonded diatomic molecules is of higher energy than the bonding $\pi 2p$ orbital, from ionization data. The energies in dinitrogen, for example, are[14] 124 kK ($\sigma_g 2p$) and 135 kK ($\pi_u 2p$). As suggested by Price,[14] a reasonable rationale for this observation is that at the short internuclear distances of the multiply-bonded molecules, the $\sigma 2p$ orbital is as much outside the nuclei as between them, and thus becomes non-bonding (but is still not a true non-bonding orbital because stretching of the molecule makes the orbital more bonding.) In keeping with this hypothesis, the O_2 molecule, with less multiple-bonding, has a much lower energy for the $\sigma 2p$ orbital. (The $\pi 2p$ orbital, on the other hand, has about the same ionization energy in all of these molecules.)

It thus seems likely that the σ-bonding interactions of molecules such as N_2 and CO which form linear metal complexes can be well described simply in terms of a non-bonding $\sigma 2p$ orbital, rather than in terms of sp hybrids. For the O_2 molecule, we would presume that the $\sigma 2p$ orbital, which is highly bonding, could not engage in such interactions.

Similar conclusions follow for metal complexes of the anions (O_2^- and O_2^{2-}) of dioxygen, as further population of the π_g orbital (with resultant O-O bond lengthening) would be expected to lower the energy of the $\sigma 2p$ orbital, while the $\pi_u 2p$ level would not be

expected to change energy drastically. The energy observed for the $^2\pi_g \rightarrow {}^2\pi_u$ transition in O_2^- incidentally shows that the $\pi_g - \pi_u$ energy separation is not greatly affected by one electron reduction.

In aqueous solution, dioxygen shows two-electron reduction to give hydrogen peroxide (or the anion HO_2^-), with the relevant reduction potentials,[18]

$$(4) \qquad \begin{aligned} O_2 + 2H^+ + 2e^- &= H_2O_2, \quad E^\circ = 0.68 \text{ v} \\ H_2O_2 + 2H^+ + 2e^- &= 2H_2O, \quad E^\circ = 1.77 \text{ v} \end{aligned}$$

showing the extremely high oxidizing strength of O_2. (In non-aqueous solution[19] O_2 shows a well-defined one-electron reduction step to give O_2^-, the ion having a half-life of at least one half-hour in pyridine, for example. The instability of O_2^- in water is related to the extremely rapid disproportionation reaction

$$(5) \qquad 2\, O_2H \rightarrow O_2 + H_2O_2$$

which seems to require availability of protons.)

The above reduction potentials may be compared with the potentials[20]

$$(6) \qquad \begin{aligned} Co(NH_3)_6^{3+} + e^- &= Co(NH_3)_6^{2+}, \quad E^\circ = 0.1 \text{ v} \\ Cu^{2+} + e^- &= Cu^+, \quad E^\circ = 0.153 \text{ v} \end{aligned}$$

and the comparison would of course indicate that O_2 is more than capable of oxidizing Cu^+ and $Co(NH_3)_6^{2+}$ in aqueous solution. The only remaining question is the partitioning of electrons in a metal ion-O_2 complex, which is one of the subjects of this thesis.

Finally, we will consider the expected bonding interactions in a variety of idealized M-O_2 geometries. A linear M-O-O unit can only show π-donor-acceptor interactions (assuming, again, that the $O_2\pi^*$ orbital is the only energetically available ligand orbital), of the type $d_{xz,yz} \rightleftharpoons \pi^*$, and is thus expected to be unstable (especially in the case, for example, of $M(d^6)$-O_2^{2-}, where there would be no bonding at all.) It is rather satisfying that there are, in fact, no known such complexes.

A bent-linear unit, on the other hand, allows strong σ-donor interactions between the π^* orbital component in the plane of the M-O_2 unit and the d_{z^2} orbital of the metal, and π-interactions between the other (out-of-plane) π^* orbital and the $d_{xz,yz}$ orbitals. These are shown in Figure I-2. For a complexed peroxide ion, these interactions could be described as being σ-donor and π-donor in character, while for a complexed O_2^- ion, π-acceptor interactions would be possible.

The interactions for a symmetrical (oxidative addition) structure are quite similar, σ-bonding being with the "$d_{x^2-y^2}$" metal orbital, and π-bonding with "$d_{xz,yz}$." These interactions are also shown in Figure II-2.

For a bent-linear metal dimer, that is, an M-O-O-M unit, we have the possibility of cis- and trans-isomers, for which the bonding is very similar, and also for planar or skewed units. For a planar unit, the bonding is similar to that in the monomer, one of the split π^* orbitals being involved in σ-bonding with both metal

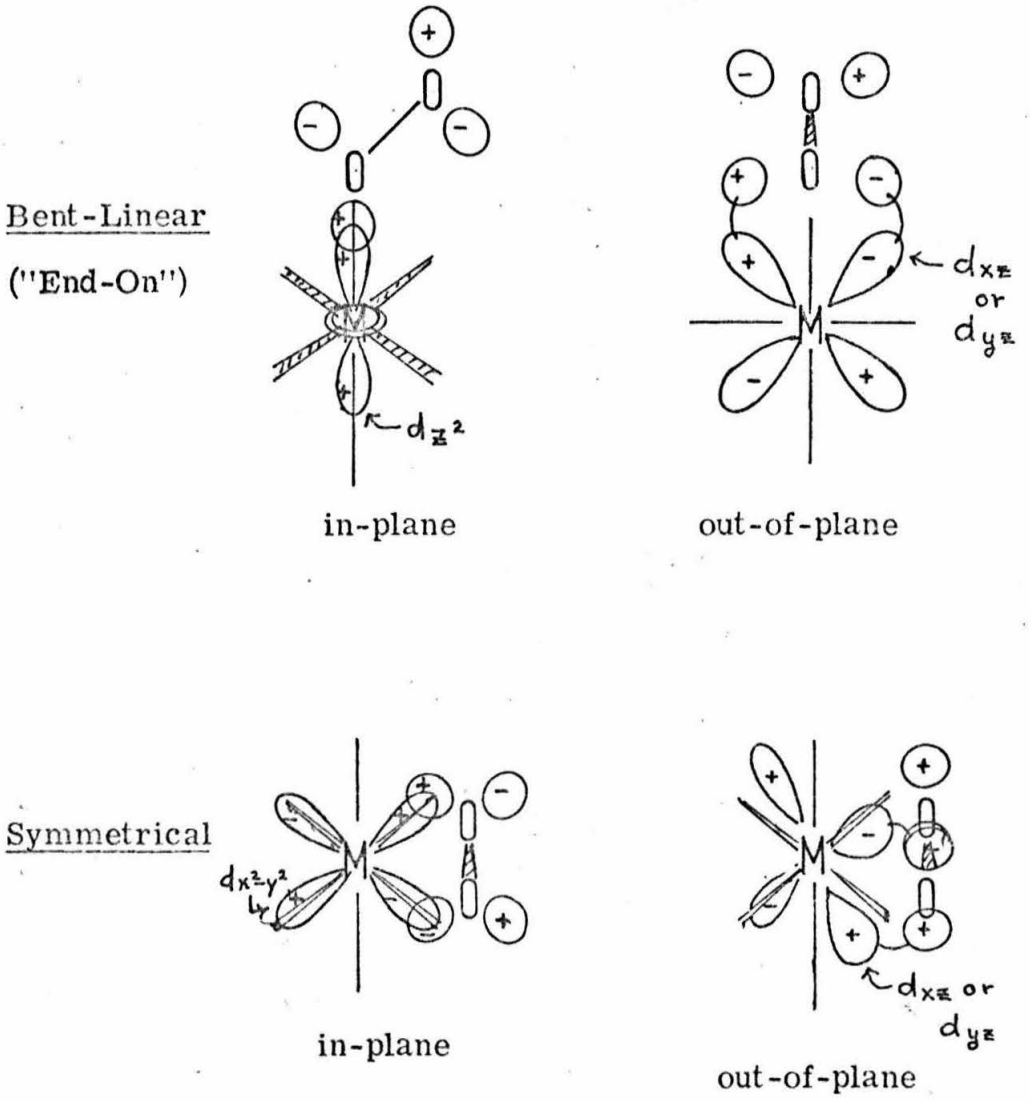


Figure I-2. Bonding interactions of O_2 with a metal ion.

centers (and the other being involved in a π-bonding with both centers.) For a skewed unit, on the other hand, the bonding would resemble that in hydrogen peroxide,[21] and each of the π^* orbitals would be (loosely speaking) involved in σ-bonding with one metal ion and π-bonding with the other. (If the preceding statement were taken literally, it would imply that the π^* orbitals would be degenerate, which is, of course, not true in the low C_2 symmetry, and the bonding and antibonding orbitals actually separate into combinations which are symmetric and antisymmetric with respect to the C_2 axis. The separation of the π^* orbitals is nevertheless expected to be much smaller for a skewed unit than for a planar unit.)

Detailed correlations of these qualitative bonding schemes with dioxygen complexes of known structure will be presented in Chapters 4 and 5, where we will also discuss the energies and selection rules for the various predicted electronic transitions in different configurations. Before we discuss the electronic spectra of dioxygen complexes, however, we must first consider the electronic structure of various structural units present in the dioxygen complexes, and this will be the subject of the following two chapters.

CHAPTER II

Octahedral Cyanide Complexes of d^6 Metal Ions

Introduction

The electronic spectra of octahedral and distorted octahedral complexes of d^6 metal ions have been the subject of innumerable investigations in this century. Indeed, much of our present understanding of the electronic structure of transition metal complexes is historically based on the study of low-spin d^6 systems, particularly the monoacidopentaammine and trans-diacidotetraammine complexes of trivalent cobalt. The ligand field treatment of the transition energies in a low-spin d^6 case is quite simple, while the experimentally observed ligand field transitions are well separated from other types of transitions in the "cobaltammine" series. The application of theory to experiment is very convincing, and forms part of the basis of modern inorganic chemistry.

For the analogous cyanide derivatives of cobalt(III), however, the situation has not been nearly as favorable. Here, ligand-field transitions are much higher in energy, resulting in considerable overlap with charge transfer absorption, while the rather large difficulties involved in obtaining the compounds in pure form have complicated matters. In addition, the fundamentally different electronic properties of cyanide ligands (versus ammonia ligands) could conceivably lead to entirely different descriptions of the ground and excited states of the complexes.

Experimental

Preparation of Compounds

$K_3[Co(CN)_5Cl]$, $K_3[Co(CN)_5Br]$, and $K_3[Co(CN)_5NO_2]$ were prepared by the method of Grassi, Haim, and Wilmarth[22] from the corresponding acidopentaammine cobalt salts. Samples were analyzed by Schwartzkopf Microanalytical Laboratory, Woodside, New York.

Analysis:

Calcd. for $K_3[Co(CN)_5Cl]$: Co, 17.24; C, 17.57; H, 0.00; N, 20.49; Cl, 10.37.

Found: Co, 17.40; C, 17.66; H, 0.00; N, 20.20; Cl, 10.39.

Calcd. for $K_3[Co(CN)_5Br]$: Co, 15.25; C, 15.54; H, 0.00; N, 18.13; Br, 20.68.

Found: Co, 15.66; C, 15.78; H, 0.00; N, 17.83; Br, 20.34.

Calcd. for $K_3[Co(CN)_5NO_2]$: Co, 16.73; C, 17.05; H, 0.00; N, 23.85.

Found: Co, 16.73; C, 18.90; H, 0.18; N, 25.03.

The $Co(CN)_5OH_2^{2-}$ ion was prepared in solution by exhaustive photolysis of an aqueous solution of $K_3[Co(CN)_6]$ at 305 nm with a UV-Products lamp. $Co(CN)_5OH^{3-}$ was obtained by making solutions prepared as above basic.

The sodium salt of trans-$Co(CN)_4(SO_3)_2^{5-}$ was obtained by a published procedure.[23] The procedure was also modified to produce the potassium salt, which was obtained as a monohydrate after drying.

Analysis:

Calcd. for $K_5[Co(CN)_4(SO_3)_2] \cdot H_2O$: C, 8.95; H, 0.89; N, 10.44; S, 11.95.

Found: C, 9.30; H, 0.40; N, 10.78; S, 10.64.

trans-$Co(CN)_4(SO_3)(OH_2)^{3-}$ was prepared in solution by dissolving trans-$K_5[Co(CN)_4(SO_3)_2] \cdot H_2O$ in 0.01 M $HClO_4$. The trans-$Co(CN)_4(SO_3)(OH)^{4-}$ ion resulted upon making solutions 0.1 M in NaOH.

$K_4[Co(CN)_5(SO_3)]$ was prepared by maintaining trans-$K_5[Co(CN)_4(SO_3)_2] \cdot H_2O$ in concentrated aqueous KCN at 70 °C for one hour and fractionally precipitating with ethanol. It was recrystallized from water with ethanol.

$Na_5[Fe(CN)_5(SO_3)] \cdot 9H_2O$ was prepared by the procedure of Hofmann.[24]

cis-$NH_4[Co(SO_3)_2(NH_3)_4] \cdot 3H_2O$ and cis-, trans-$NH_4[Co(SO_3)_2(en)(NH_3)_2] \cdot 2H_2O$ were prepared by the method of Bailar and Peppard.[25]

trans-$Na[Co(SO_3)_2(en)_2]$ was prepared by the method of Baldwin.[26]

$K[Co(CN)_4en] \cdot H_2O$ was prepared by the method of Maki and Okawa.[27]

trans-$K[Rh(SO_3)_2(NH_3)_4]$ was prepared by refluxing $[Rh(NH_3)_5OH_2](ClO_4)_3$ in concentrated K_2SO_3 solution (first filtering off the $KClO_4$ precipitate), and fractionally precipitated with ethanol. No attempt was made to obtain an analytically pure sample.

Spectroscopic Measurements

Ultraviolet, visible, and near-infrared spectral measurements were made on a Cary Model 17 spectrophotometer. Spectra at 77°K were measured in a quartz dewar with optical quality windows, samples being completely immersed in liquid nitrogen. Prior to measurements, the liquid nitrogen was super-cooled by pumping or by blowing helium gas through the liquid, in order to avoid bubbling. The cells for these measurements were made by molding round quartz tubing on a square molybdenum frame, rounded corners helping to avoid crack formation in glassed solvents. The solvent used in most runs was a 1 : 1 mixture of saturated LiCl solution and water, pH being adjustable with added HCl, H_2SO_4, or LiOH. Some runs were also done using a 9 : 10 saturated $MgCl : H_2O$ mixture, which had similar properties. Spectra were routinely corrected by taking baseline measurements using solvent alone at both room temperature and 77°K. Measurements on the same solutions were also done in commercial suprasil square cells at room temperature, in order to correct for path-length variability of the "homemade" cells. Molar extinction coefficients at 77°K were corrected for volume contraction, the correction factors being 2.5% for the LiCl solvent, and 10% for the $MgCl_2$ solvent.

Infrared spectra of solid compounds as Nujol mulls and KBr pellets were measured on a Perkin-Elmer Model 225 grating spectrophotometer.

Photochemical Measurements

Samples were irradiated using merry-go-rounds.[28] In various experiments, different filter systems were used to isolate the groups of lines near 254, 313, 366, or 436 nm in the mercury lamp spectrum. Light intensities were measured using ferrioxalate actinometry.[29] Three ml samples were used, light intensities being of the order of 10^{-7} einsteins min^{-1}. Correction for thermal aquation of trans-$Co(CN)_4(SO_3)_2^{5-}$ was done by measuring rates in parallel control experiments. The other complexes investigated were thermally inert under the reaction conditions.

Disappearance of trans-$Co(CN)_4(SO_3)_2^{5-}$ was monitored by following the decrease in absorbance at 317 nm. Monosulfito complexes were monitored at 260 nm. All analyses and sample preparations were carried out in darkened rooms. Spectrophotometric analysis was done with a Beckman DU spectrometer.

Formation of Co(II) was detected by addition of 6 M NH_4SCN mixtures. Formation of the blue $Co(NCS)_4^{2-}$ ion (absorption maximum at 623 nm) was determined spectrophotometrically, with calibration of the system employing known concentrations of $CoCl_2 \cdot 6H_2O$ in the same solvents.

Quenching of the aquation of trans-$Co(CN)_4(SO_3)_2^{5-}$ was studied by observing the effect of added K_2SO_3 on photoaquation rates.

Results and Discussion

Ligand Field Spectra

An octahedral low-spin complex of cobalt(III) is expected to show two low-lying spin-allowed ligand field transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, both excited states arising from the $t_{2g}^5 e_g$ configuration. Lowering of the molecular symmetry to C_{4v}, as in a mono-substituted complex, causes the first transition to split into $^1A_1 \rightarrow {}^1E^a$ and $^1A_1 \rightarrow {}^1A_2$, while the second splits into $^1A_1 \rightarrow {}^1E^b$ and $^1A_1 \rightarrow {}^1B_2$. Within the crystal field formalism, the splittings of these states may be expressed in terms of two parameters, Ds and Dt (we choose the parameterization of Ballhausen[30]), together with the usual 10 Dq. In this scheme, the energy of the $^1A_1 \rightarrow {}^1A_2$ transition is found to be independent of either Ds or Dt, while the $^1A_1 \rightarrow {}^1E^a$ transition depends on Dt, and the $^1A_1 \rightarrow {}^1B_2$ and $^1A_1 \rightarrow {}^1E^b$ transitions depend on both parameters. Extension of this model requires further assumptions. If we assume approximate transferability of certain radial integrals from the unsubstituted (parent) complex to its mono-substituted derivatives, then Dq, which depends on the in-plane field strength, should be roughly invariant from complex to complex; thus a series of mono-substituted complexes should show a $^1A_1 \rightarrow {}^1A_2$ transition

at the energy of the $^1A_1 \rightarrow {}^1T_{1g}$ transition of the parent, and a $^1A_1 \rightarrow {}^1E^a$ transition moving to higher or lower energy as a function of Dt. Furthermore, within the point-charge model we can express Dt as a function of the difference in Dq's of the two different ligands.

Cobaltammine complexes are found to obey this model extremely well in a qualitative sense, and even reasonably well quantitatively.[31] Thus, Dq's evaluated from the empirical Dt parameter (from the splitting of the first two ligand field bands) are found to be roughly transferable from complex to complex, and compare reasonably well to the values of 10 Dq from the spectra of the octahedral complexes, where these are known. This systematic variation of the "first" ($^1A_1 \rightarrow {}^1E^a$) band of these complexes formed the original basis of the spectrochemical series.[32]

We should naively expect the monoacido pentacyanocobaltates to behave similarly. Here, 10 Dq for the parent complex is much larger (34.5 kK[33] versus 24.9 kK[31]) hence we expect larger splittings (larger differences in Dq) so that, if anything, assignments should be easier. Experimentally, the problem is far from simple. The d-d bands in the pentacyano series are at rather high energy (the compounds are generally light yellow) and overlap considerably with tails of intense charge-transfer bands. In most of these complexes, only one d-d band can be seen, making theories necessarily based on observation of more than one band difficult to apply.

Compounding our difficulties, we know in the beginning that cyanide is, at least potentially, a much different ligand from ammonia. NH_3 is a purely σ-bonding ligand, while CN^- is a strong π-acceptor, at least in its complexes with low-valent metal ions. This π-accepting character is reflected in the increase in Δ of the hexacyanide over the hexaammine. We intuitively associate splitting of the octahedral t_{2g} orbitals with differences in π-bonding ligand interactions, and splitting of the e_g orbitals with differences in σ-bonding interactions (this is reflected more directly in the alternative parameterization of the angular overlap model[34]) so that we might expect a rather different splitting pattern in the cyanide complexes. Given what must be described as a "fortunate" agreement of the previously outlined theory with experiment in the case of the ammine complexes, we cannot be extraordinarly confident that it will also apply here.

Gutterman,[35] after careful spectral examination of the series $Co(CN)_5X^{3-}$, $X^- = NCS^-$, SCN^-, $NCSe^-$, and N_3^-, was led to propose that the single ligand field band observed was an unsplit "$^1A_{1g} \rightarrow {}^1T_{1g}$" transition, as no clear evidence of splitting appeared in any of her spectra, and found some support for this analysis in magnetic measurements on the corresponding Fe(III) $(CN)_5X^{3-}$ complexes which indicated a rather small splitting of the ground state $^2T_{2g}$ (d^5) term. This was proposed as being consistent with a model in which the cyanide ligands dominated the electronic structure of the complexes, the electronic states being effectively

octahedral, with slightly reduced "average" Δ. Indeed, both the photo- and thermal chemistry of the $Co(CN)_5X^{3-}$ complexes lends itself to such a model, consisting in both cases entirely of the pure dissociative substitution of X^-. (We shall later discuss the photochemistry in more precise terms.)

However, we mildly note at this point that the aforementioned crystal field model, in fact, predicts only a small splitting of the t_{2g} orbitals. This splitting amounts to 5 Dt-3 Ds, which in the Fe(III) case corresponds to an actual splitting between two states, $^2B_2$ and ^2E. Inserting "reasonable" values for the parameters, we predict a splitting on the order of -500 to 1000 cm^{-1}, certainly consistent with the magnetic results. (By "reasonable" values, we mean values derived from a variety of studies on similar complexes of Co(III)[31] and Cr(III),[36] as well as values consistent with results to be presented later in this chapter.) On the other hand, the splitting of the e_g orbitals is 5 Dt + 4Ds, which may be considerably larger. (Large splittings of the d_{z^2} and $d_{x^2-y^2}$ orbitals are intuitively reasonable for monosubstituted complexes.) Furthermore, transitions between the upper and lower d-manifolds involve various differences of splitting parameters, and can show even larger splittings.

An additional interesting point is that the spectra of the mixed cyanoaquo complexes of Cr(III),[36] which are free of charge-transfer interference in the d-d region, fit our model quite nicely. This would seem to indicate that, at least for Cr(III), cyanide is not a very unusual ligand.

We, therefore, reinvestigated the acidopentacyanocobaltate series, with an emphasis on those complexes where charge transfer absorption was of rather high energy. Our aim in doing this was not to "explain" the spectra by a theoretical model, although we were quite willing to accept a model if such proved feasible, but simply to find the best simple description we could of the lowest excited states of these complexes, both to aid in understanding the reactivity patterns of these excited states, and to assist in the interpretation of the more complicated spectra of complexes having other types of low-lying excited states in addition to ligand-field states.

The $Co(CN)_5NH_3^{2-}$ ion[37] is an ideal example of a pentacyanocobaltate complex having no low-energy charge-transfer absorption, but suffers from a rather low value of Dt, as might have been predicted. In the cobaltammine series, $Co(NH_3)_5OH_2^{3+}$ is quite analogous, showing two apparently unsplit ligand field bands, both somewhat red-shifted from the hexaammine positions. $Co(CN)_5NH_3^{2-}$ similarly shows two ligand field bands, at 345 nm and 268 nm, red-shifted from the $Co(CN)_6^{3-}$ bands at 312 nm and 260 nm. The two bands are of comparable intensity, and the 345 nm band is broad and somewhat asymmetric towards higher energy. The high energy band (268 nm) is readily assigned to $^1A_1 \rightarrow \{^1B_2, {}^1E^b\}$. The corresponding band in $Co(NH_3)_5X^{2+}$ complexes is never observed to split and generally shifts only moderately to lower energy. One may assume that the splitting

of the $^1T_2$ state fortuitously cancels. (Polarized crystal data[38] support this analysis, bands being observed in different polarizations with small energy differences. Polarized spectra of trans-diacidotetraammines[39] show relatively large splittings of the $^1B_2$ and $^1E^b$ states, and are of interest in that they provide estimates of the parameter Ds.)

The lack of observable splitting in the low-energy band ($^1A_1 \rightarrow \{^1E^a, {}^1A_2\}$) can be attributed to the small shift of the $^1E^a$ component to lower energy, and also, partially, to the expected unequal oscillator strengths of the two components. The $^1A_1 \rightarrow {}^1E^a$ transition is formally orbitally allowed in C_{4v} symmetry, as well as being strongly vibronically allowed, while the $^1A_1 \rightarrow {}^1A_2$ transition is only weakly vibronically allowed, mainly via coupling with equatorial metal-cyanide stretching modes. Thus, the $^1A_1 \rightarrow {}^1A_2$ band, which is the band we expected at approximately 312 nm, could easily be hidden in the tail of the strong, nearby $^1A_1 \rightarrow {}^1E^a$ component. (Actually, a similar analysis holds for the $^1A_1 \rightarrow \{^1B_2, {}^1E^b\}$ band, so long as the splitting remains relatively small.)

A somewhat larger splitting is expected in the $Co(CN)_5OH_2^{2-}$ ion, and here we do see evidence of a weak second component. This ion cannot be isolated as a solid salt without extensive decomposition.[40] However, in agreement with past workers,[41] we have found that it may be formed cleanly and quantitatively by photolysis of $Co(CN)_6^{3-}$ in dilute aqueous solution. The electronic spectrum, shown in figure II-1, shows a distinct shoulder at ~ 310 nm at

room temperature, the oscillator strength being roughly one-third of that of the low energy band at 380 nm, and we are prompted to identify this as the $^1A_1 \rightarrow {}^1A_2$ transition.

Figure II-1 also shows the spectrum we obtain for the $Co(CN)_5OH^{3-}$ ion, which has a definite maximum at 290 nm which might be assigned either to $^1A_1 \rightarrow {}^1A_2$ or to $^1A_1 \rightarrow$ "$^1T_2$". However, the slowness with which the spectrum of the aquo ion changes upon being put in basic solution (although the change is reversible) leads us to suspect polymerization. Solutions of the hydroxo complex do decompose irreversibly on standing. Indeed, the early onset of charge-transfer absorption in the aquo spectrum is somewhat surprising, and perhaps suggests some small concentration of other (polymerized) complexes, polymerization being known to occur upon concentration of aquo solutions. (The resulting species may be analogous to the dimers $Fe_2(CN)_{10}^{n-}$ known to form in the pentacyanoaquo Fe(II) and Fe(III) systems.[42]) Given this residual doubt we cannot be completely confident about the $Co(CN)_5OH_2^{2-}$ assignments.

However, in figure II-2, we show the spectrum of $Co(CN)_5Cl^{3-}$ at room temperature and 77°K. We observe a shoulder at room temperature at ~320 nm, sharpening into a peak at 313 nm at 77°K. The weak peak has an integrated intensity of less than a third of that of the ligand field peak at 391 nm, and we feel confident in assigning the two peaks as the $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E^a$ transitions. Great efforts were taken to ensure the purity of the complex,

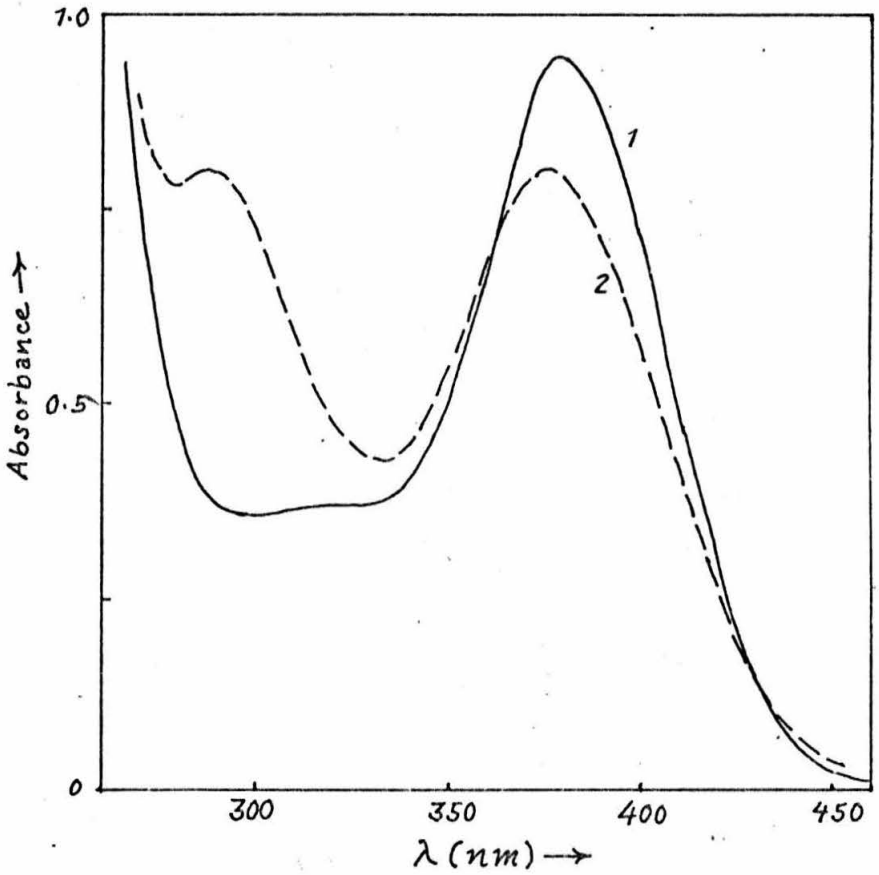


Figure II-1. Electronic absorption spectra of $Co(CN)_5OH_2^{2-}$ (1) and $Co(CN)_5OH^{3-}$ (2), 3.3×10^{-3} M in aqueous solution, R.T.

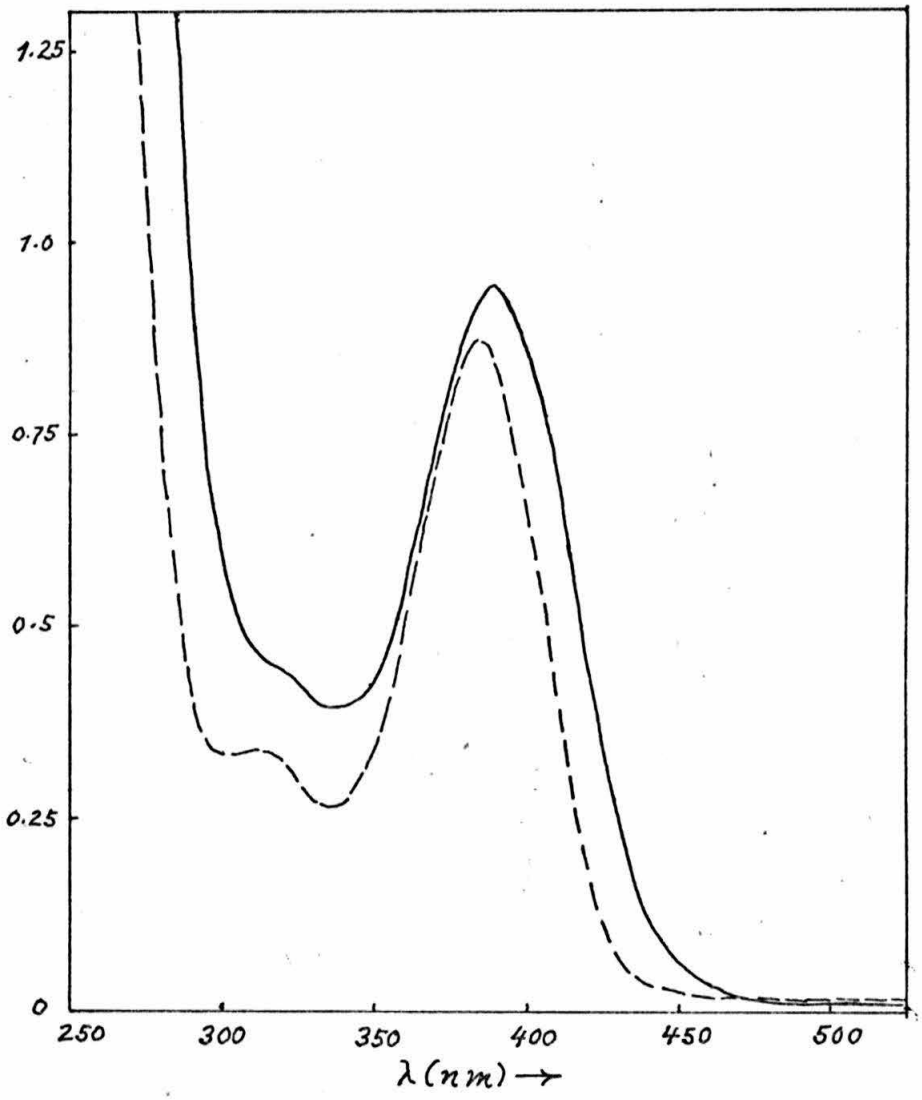


Figure II-2. Electronic spectrum of $K_3[Co(CN)_5Cl]$, 4.64×10^{-3} M in 50% saturated aqueous LiCl at R.T. (——) and 78°K (----).

particularly in regard to avoiding possible contamination with the hexacyanide, and all analytical methods, including elemental analysis and infrared spectroscopy, as well as agreement of our peak ϵ at room temperature with the most reliable literature value[43] indicate conclusively that the 320 nm peak is an authentic peak of $Co(CN)_5Cl^{3-}$.

We note in passing that the $^1A_1 \rightarrow {}^1E^a$ transition is observed to have an ϵ of only 200, while the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of $Co(CN)_6^{3-}$, which is LaPorte forbidden, has an ϵ of 190. This implies that the formally orbitally allowed nature of the former transition does not make a large contribution to its intensity. The transition was strongly vibronically allowed in octahedral symmetry and remains so in C_{4v}. The temperature behavior of the band confirms that the majority of its intensity is vibronic in origin, as the oscillator strength decreases at lower temperature. Ballhausen[44] has made similar observations on other metal complexes. This situation can be readily rationalized, as, no matter how low the symmetry of the complex, ligand field transitions remain effectively forbidden, because of the nature of the orbitals involved, unless other orbitals (ligand orbitals or metal p orbitals, for example) are heavily mixed in with the d orbitals.

We have also attempted to prepare several other complexes of ligands which would combine large Dt values and high energy charge-transfer characteristics with relatively little success. These were all complexes of relatively "hard" anions and bases,

almost necessarily in order to fit the preceding requirements, and all proved to have rather low stability. Thus, the acetate, although we had some success in preparing it, could not be maintained in a pure enough state for reliable spectral measurements, while the fluoride showed no evidence of existing at all. We are thus left with those $Co(CN)_5X^{3-}$ complexes for which we have already indicated that charge-transfer obliterates most of the ligand field spectrum. Actually, having now been given some indication of what we are looking for (a relatively weak band at 30-31 kK), we can recognize the probable presence of such a band in most acidopentacyanocobaltate spectra. A particularly pleasing example is the 77°K spectrum of $Co(CN)_5NCS^{3-}$,[35] which shows clear evidence of a weak band at ~ 30 kK.

Similarly, the appearance of many of our spectra suggests, but does not unambiguously establish, the presence of a band at ~ 275 nm, presumably corresponding to the $^1A_1 \rightarrow \{^1E^b, {}^1B_2\}$ transition. The lack of positive identification of this band in most $Co(CN)_5X^{n-}$ spectra presents us with a possible ambiguity in the identification of a "second band." However, the $^1A_1 \rightarrow \{^1E^b, {}^1B_2\}$ transition is expected to be of comparable intensity to the $^1A_1 \rightarrow {}^1E^a$ transition (and is, where observed) so that we feel justified in our identifications of the $^1A_1 \rightarrow {}^1A_2$ transition.

We find further support of our assignments in the spectra of multi-substituted cobalt cyanide complexes. Extending the reasoning we outlined in the beginning of this chapter to more highly

Table II-1

Ligand Field Transitions of

Selected $Co(CN)_5X^{n-}$ Complexes[a]

X	Assignment	λ (nm)	$\bar{\nu}$ (kK)	ϵ
CN^- [37]	$^1A_{1g} \rightarrow {}^1T_{1g}$	312	32.1	191
	$^1A_{1g} \rightarrow {}^1T_{2g}$	257	38.9	130
SO_3^{2-}	$^1A_1 \rightarrow {}^1E^a$	335	29.9	430
NO_2^-	$^1A_1 \rightarrow {}^1E^a$	~345 (sh)	29.0	490
NH_3 [37]	$^1A_1 \rightarrow {}^1E^a$	345	29.0	250
	$^1A_1 \rightarrow \{{}^1E^b, {}^1B_2\}$	268	37.3	155
OH_2	$^1A_1 \rightarrow {}^1E^a$	380	26.3	280
	$^1A_1 \rightarrow {}^1A_2$	~310 (sh)	32.3	110
Cl^-	$^1A_1 \rightarrow {}^1E^a$	392	25.5	200
	$^1A_1 \rightarrow {}^1A_2$	~316 (sh)	31.7	97

[a] Aqueous solution at room temperature.

substituted complexes, we can generate the diagram shown in figure II-3, showing the behavior of the $^1T_{1g}$ octahedral state with increasing substitution. (The energy scale is linear.) The rather pleasing pattern of the diagram is mainly a consequence of the principle of holohedral symmetry.[35] The (rather well-known from cobaltammine spectra) predictions of main interest to us are that, for trans-disubstituted complexes, the splitting of the $^1T_{1g}$ state simply doubles, while for cis-disubstituted complexes, the ^1E state remains at the same energy as in the mono-substituted complex, while the weak $^1A_2$ band now moves to lower energy.

In figure II-4, we show the spectra of $Co(CN)_5SO_3^{4-}$ and trans-$Co(CN)_4(SO_3)_2^{5-}$. The monosulfito $^1A_1 \rightarrow {}^1E^a$ band at 335 nm corresponds to a splitting of 2.6 kK, assuming a $^1A_2$ band at 312 nm, while the disulfito transition at ~ 375 nm similarly corresponds to a splitting of 5.4 kK, in rather close agreement with the expected doubling.

The spectrum of $Co(CN)_4en^-$ [46] shows a maximum at 352 nm, comparing nicely to the $^1A_1 \rightarrow {}^1E^a$ band of $Co(CN)_5NH_3^{2-}$ at 345 nm. Here, the small shift to lower energy is not inconsistent with the presence of a weak $^1A_2$ band at lower energy.

Thus, for these complexes, we can demonstrate the apparent applicability of our assignments simply by comparison to the mono-substituted analogues, without direct observation of a transition to $^1A_2$. A variety of other cyanide substituted cobaltammines have been reported,[46] and the observed spectra are all quite consistent with figure II-3.

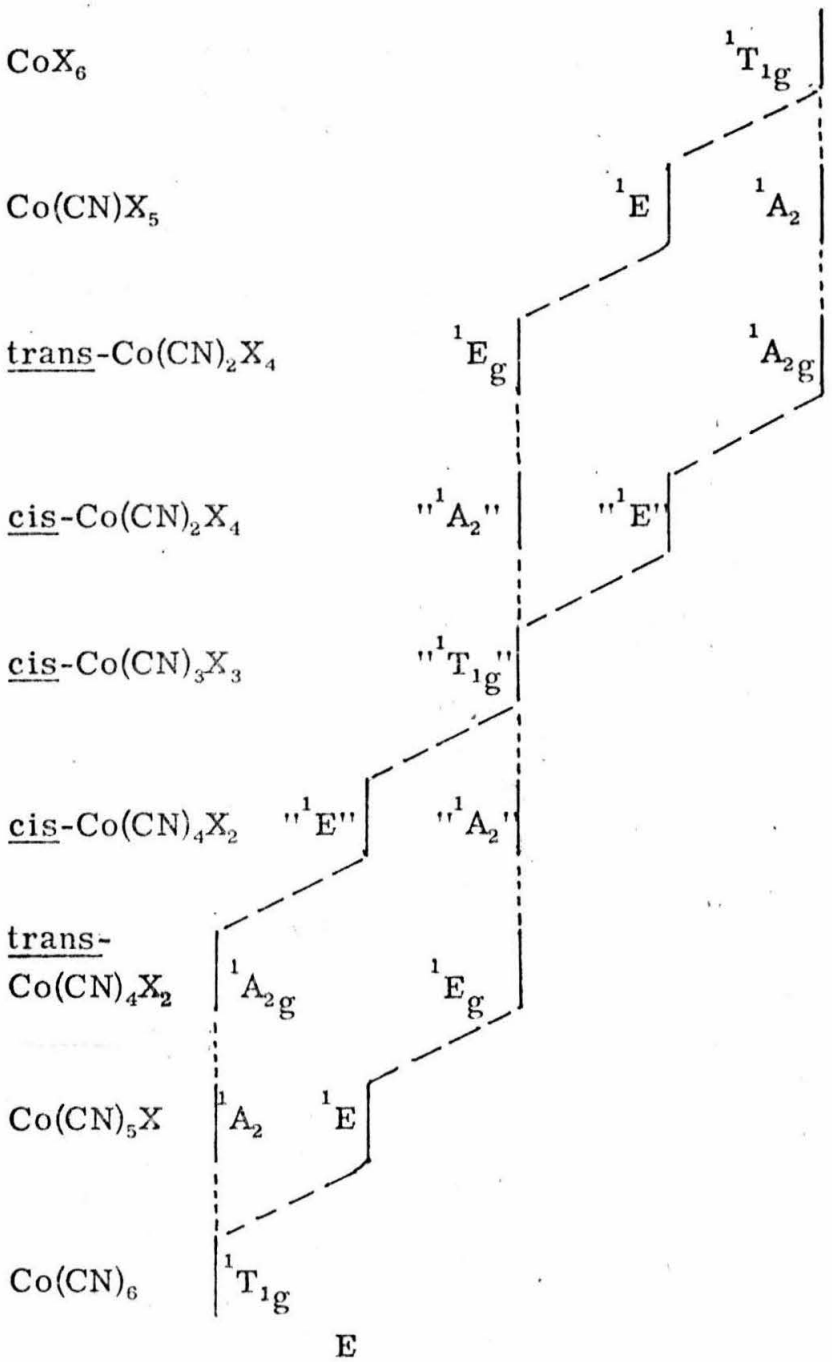


Figure II-3. Splitting of $^1T_{1g}$ (d^6) in fields of lower symmetry. Ligand field strength of X < ligand field strength of CN^-.

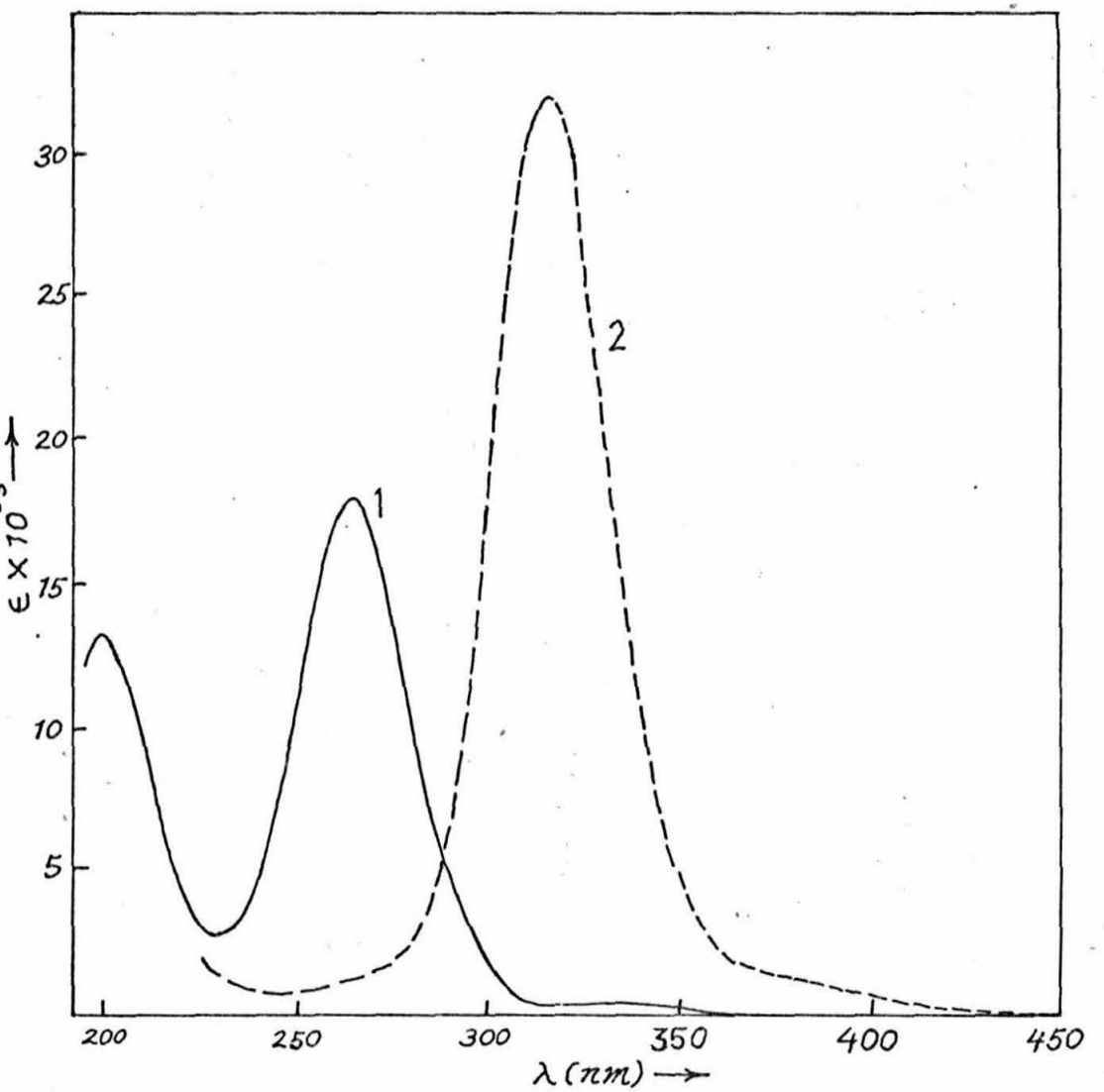


Figure II-4. Electronic spectra of $Co(CN)_5SO_3^{4-}$ in water (1) and <u>trans</u>-$Co(CN)_4(SO_3)_2^{5-}$ in 1<u>M</u> NaOH (2).

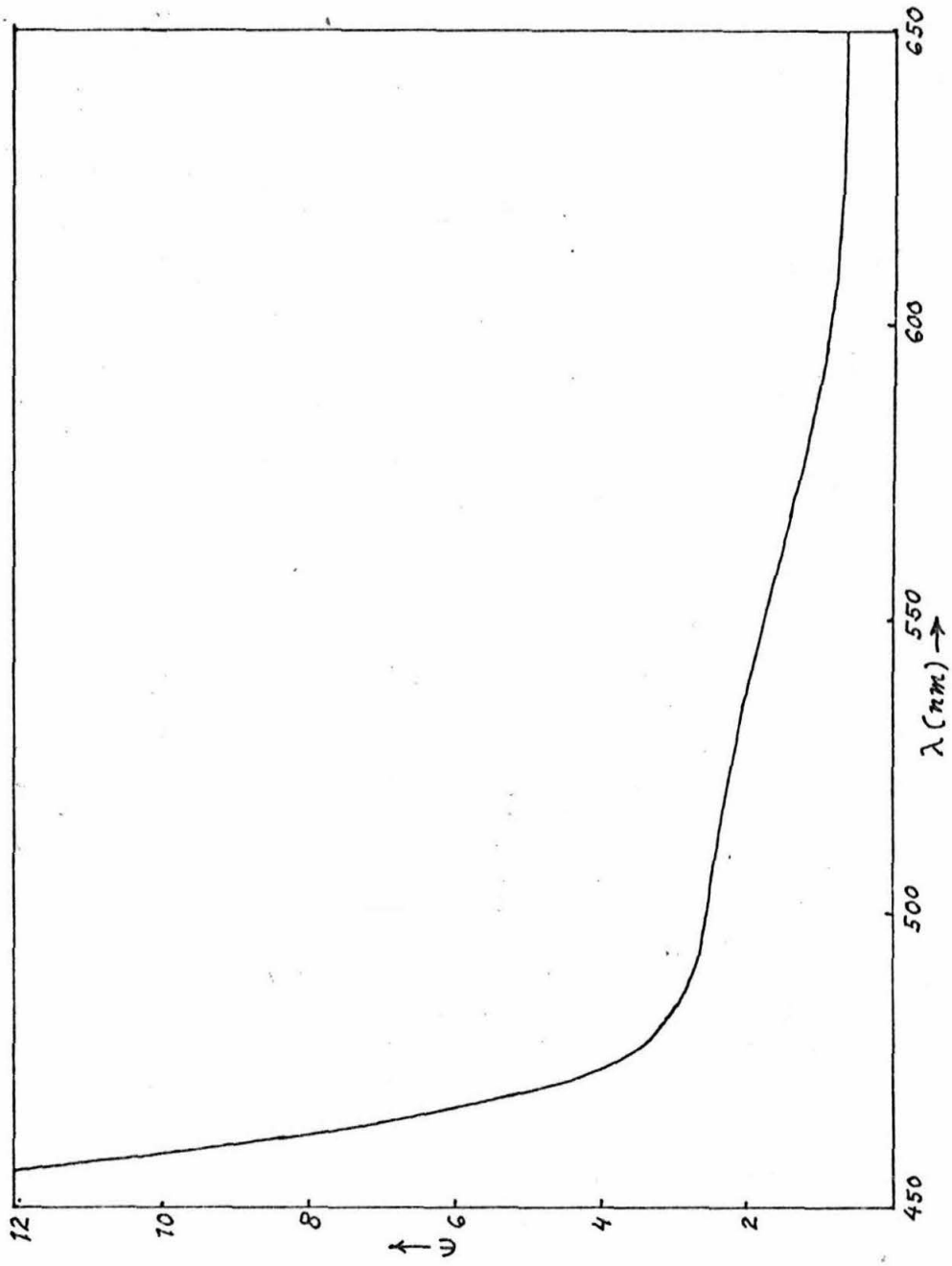


Figure II-5. $K_3Co(CN)_5Cl$ in aqueous solution, R.T.

Finally, we find a linear correlation between the energies of the lowest ligand field bands of acidopentaamminecobalt complexes and acidopentacyanocobaltates. Such a correlation strongly implies that the assignments of the bands are similar. This correlation necessarily also leads to a correlation of Dq values, calculated by the method of reference 31, but more strongly, the agreement between Dq's for the two series is relatively good, $Co(CN)_5Cl^{3-}$ giving a calculated Dq of 1400 cm^{-1} for chloride, for example, in good agreement with 1560 cm^{-1} for chloride in $Co(NH_3)_5Cl^{2+}$.[31] The calculated Dq's in the pentacyano series are generally somewhat lower than the pentaammine values, which is not unreasonable, as most of our ligands are π-donors. Capability for π-donor interactions, usually associated with the low end of the spectrochemical series, might be expected to be accentuated in complexes of the strong π-acceptor cyanide. (This is in harmony with the usual classification of the $Co(CN)_5^{2-}$ unit as being "soft".)

As implied by the above, the spectrochemical series observed for the acidopentacyanocobaltates is in agreement with that observed for acidopentaamminecobalt complexes, with some slight deviations consisting of ligands, notably S-bound thiocyanate, moving slightly lower in the cyanide series, indicating a disproportionately increased π-donor capability.

The pentacyano complexes of iridium(III) and rhodium(III) have recently been investigated in these laboratories by Greg Geoffroy.[47] For these complexes, which have even higher

energy d-d bands, the problem of charge-transfer overlap becomes sufficiently severe that second and third ligand-field bands cannot be seen in the spectra of any derivative. However, the data on the $^1A_1 \rightarrow {}^1E^a$ band is of interest in that we observe a large shift in the spectrochemical series, s-bound thiocyanate moving between Br^- and I^- for Rh(III), and moving to lower than I^- for Ir(III). This is consistent with an increase in π-donor capability as the size of the central metal ion increases (increasing overlap of d-orbitals with the primarily sulfur-localized thiocyanate 2π orbital.) Trends of this sort, with potentially strongly π-donating ligands moving to anomalously low positions in the spectrochemical series of a "soft" metal ion, can probably be expected to be quite general.

The iridium complexes are also of interest in that singlet-triplet transitions, presumably $^1A_1 \rightarrow {}^3E^a$, are observed at energies 5-6 kK less than the $^1A_1 \rightarrow {}^1E^a$ transitions, with observed ϵ's of the order of 60-200, the intensities being an expected consequence of the "heavy-atom" effect. Theoretically, the energy difference between $^1A_1 \rightarrow {}^1E^a$ and $^1A_1 \rightarrow {}^3E^a$ should be 2C, which has been estimated to be about 5.4 kK for $Co(CN)_6^{3-}$.[33] For comparison, we have also observed a very weak shoulder at ~525 nm, $\epsilon \sim 2$, in the spectrum of $Co(CN)_5Cl^{3-}$, as shown in figure II-5, and feel fairly confident that this is a real singlet-triplet absorption. The energy splitting between the $^1E^a$ and $^3E^a$ bands is ~6.5 kK, leading to $C \simeq 3300\ cm^{-1}$.

In conclusion, we find that the ligand field bands of substituted cobalt(III) cyanide complexes follow the same patterns which have been well established for substituted cobalt(III) ammine complexes, and that we can therefore estimate energies for ligand field excited states of these complexes even when charge-transfer absorption makes them unobservable. We further note that energy estimates allow us to evaluate the mixing of the two ^1E excited states in the tetragonal field which is found to be small, so that we can realistically label the transitions to these states as $d_{xz,yz} \rightarrow d_{z^2}$ and $d_{xz,yz} \rightarrow d_{x^2-y^2}$, in order of increasing energy, an identification which will be useful in discussing the photochemistry of the complexes.

Charge-Transfer Spectra

The charge-transfer spectra of substituted cobaltammines have been subjected to rather less analysis than the ligand field spectra. A primary reason for this is the rather more complicated (in terms of the number of parameters) nature of the theory of these transitions, the best method of handling them at present being the "optical electronegativity" method of C. K. Jørgensen.[48] Unfortunately, this method, while an effective tool for hexahalide complexes, is rather ineffective, and quite inexact, at any rate, when applied to complexes such as those we are considering. We shall therefore consider these transitions rather qualitatively.

For mono- or trans-dihalo derivatives, we expect two ligand-to-metal charge-transfer transitions into the "e_g" metal

orbitals, "σ" charge-transfer from the halogen p_z (a_1) orbital, and "π" charge-transfer from the halogen p_x, p_y (e) orbitals. (In trans-disubstituted complexes, there are symmetric and antisymmetric combinations, a_{1g}, a_{1u} and e_g, e_u, only the antisymmetric combinations giving LaPorte allowed transitions.) The σ charge-transfer transition, $^1A_1 \rightarrow {}^1A_1$ ($p_z(X^-) \rightarrow d_{z^2}(M)$, with the $p_z \rightarrow d_{x^2-y^2}$ transition being orbitally forbidden) is quite intense, being a $\sigma \rightarrow \sigma^*$ transition with large overlap. A halide π-type transition, on the other hand, is generally much weaker, being essentially a non-bonding to antibonding transition with poor overlap, although, with ε's having a lower limit of ~500, it is still generally distinguishable from ligand field absorption.

In pseudohalide derivatives, such as thiocyanate and azido complexes, we expect to observe ligand-to-metal charge-transfer from the non-bonding 2π orbital, with the σ charge-transfer usually expected to be quite high-energy. (In cases where the metal-pseudohalide linkage is non-linear, we may expect the 2π level to split, and a possibility then exists for observing two such L → M transitions.) Pseudohalide π charge-transfer is of somewhat variable intensity, being, for example, of the order of halide π charge-transfer for N-bonded thiocyanate, but of the order of halide σ charge-transfer for s-bonded thiocyanate. (This is explicable in terms of the much greater spatial overlap of the thiocyanate 2π orbital for s-bonding, and also because of the distinctly non-linear Co-thiocyanate bond. The transition thus takes on much of the character of a $\sigma \rightarrow \sigma^*$ transition.)

In table II-2, we show a summary of charge-transfer energies and peak ϵ's for some acido pentaammine cobalt complexes, as well as for the corresponding acidopentacyano-cobaltates, while in figure II-6, we show the charge-transfer spectra of $Co(CN)_5Br^{3-}$ and $Co(CN)_5Cl^{3-}$, which have not previously been reported.

The halopentacyanocobaltates show the expected two bands, shifted to higher energy relative to the pentaammines by 2000 to 4000 cm^{-1}. We predict two components for the π-charge transfer in these complexes, corresponding to the two ^1E states resulting from excitation into either the d_{z^2} or $d_{x^2-y^2}$ metal orbital, and can estimate the expected splitting of these states as 4 Ds + 4 Dt, the splitting of the $^2A_1$ and $^2B_1$ states of a low-spin d^7 system in a C_{4V} field. As an example, taking Dt = 0.54 kK, the value appropriate for $Co(CN)_5Cl^{3-}$, and taking Ds $\cong$ Dt, we estimate the splitting to be ~ 5000 cm^{-1}, which should certainly be observable. As we do not observe any splitting, we suggest that we are seeing only the $e \rightarrow d_{z^2}$ component, with the $e \rightarrow d_{x^2-y^2}$ component hidden under the σ-charge transfer, a situation analogous to that prevailing for the ligand field spectra. We can unambiguously eliminate an assignment of the observed π-transition as $e \rightarrow d_{x^2-y^2}$ (with, perhaps, a very weak and unobserved $e \rightarrow d_{z^2}$ transition) because for such an assignment the difference in energy between the σ- and π-transitions would be expected to decrease along the series Cl^-, Br^-, I^-, as a result of increased $d_{x^2-y^2} - d_{z^2}$ splitting. In contrast

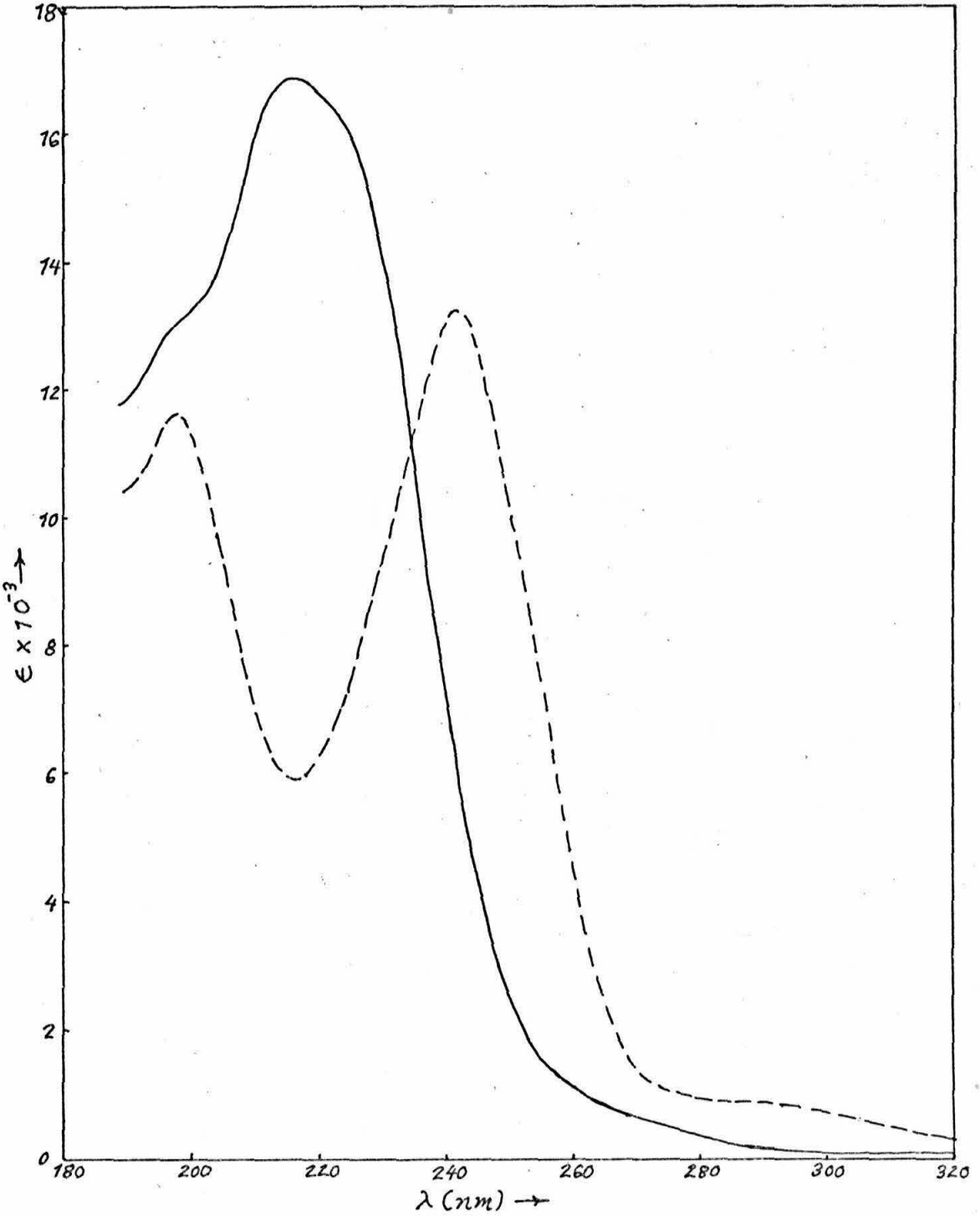


Figure II-6. UV spectra in aqueous solution of $Co(CN)_5Cl^{3-}$ (——) and $Co(CN)_5Br$(----).

Table II-2

Charge Transfer Maxima of Mono-Substituted Co(III) Complexes in Aqueous Solution

		$Co(CN)_5X^{3-}$			$Co(NH_3)_5X^{2+}$		
X^-	Assignment	$\bar{\nu}$ (kK)	ϵ	ref	$\bar{\nu}$ (kK)	ϵ	ref
Cl^-	$\pi \rightarrow d_{z^2}$	37.7	866	a	36.0	400	49
	$\sigma \rightarrow d_{z^2}$	44.6	16,100	a	43.9	12,900	49
Br^-	$\pi \rightarrow d_{z^2}$	33.9	822	a	31.8	560	49
	$\sigma \rightarrow d_{z^2}$	41.3	13,210	a	39.5	12,600	49
I^-	$\pi \rightarrow d_{z^2}$	30.3	2,950	41	26.1	1.450	49
	$\sigma \rightarrow d_{z^2}$	38.5	17,500	41	34.9	12,600	49
NCS^-	$\pi \rightarrow d_{z^2}$	37.7	2,340	35	32.7	1,550	50
	$\pi \rightarrow d_{x^2-y^2}$	44.0	6,200	35	--	--	--
SCN^-	$\pi \rightarrow d_{z^2}$	37.7	17,100	35	34.7	15,600	51
	$\pi \rightarrow d_{x^2-y^2}$	44.0	4,300	35	---	--	--
NO_2^-	MLCT	35.2	2,700	a	30.7	1,590	52
	LMCT	43.7	22,700	a	42.0	9,400	52
SO_3^{2-}	$\sigma \rightarrow d_{z^2}$	37.7	18,100	a	36.5	12,000	52

[a] This work.

this difference increases very slightly along the series, quite in keeping with results for hexahalometalate complexes,[48] and also with the trend in the ammine complexes.

The shift of the charge-transfer to higher energy in the cyano complexes (relative to the ammine complexes) is thus not, even loosely speaking, a simple function of the increase in Δ, the increase in the d σ^* splitting for the cyanide complexes tending to partially counteract this increase. This at least in some measure accounts for the observation (implicitly noted in the previous section) that the difference in energy of charge-transfer and ligand-field absorption is decreased in the cyano complexes. The difference in energy of the σ- and π-transitions is, on the other hand, relatively constant in the two series of complexes, simply because we are observing transitions to d_{z^2} in all cases. The σ-π splitting is generally about 500 cm^{-1} smaller in the cyano complexes, and this rather small but systematic energy difference may indicate greater bonding character of the halide π-orbital in the cyano complexes (that is, that the π-donor capability of the halides is more important).

In the case of the pseudohalide derivatives, we have no interference from σ-charge transfer, and here we detect a weaker component of the π charge transfer at 6000 to 9000 cm^{-1} higher energy. In the case of the SCN^- derivative, this is a well-resolved peak at 44.0 kK, $\epsilon = 4,300$, whereas the main charge transfer transition at 37.7 kK has $\epsilon = 17,100$. In other derivatives, we see

a more or less well resolved shoulder. This peak has previously been assigned[35] as the low energy component of the ligand $2\pi \rightarrow 3\pi$ transition, which occurs at about this energy in the free ligand. However, π-donor interaction, especially in the case of the SCN^- derivative, would tend to raise the energy of this transition, hence we feel our present assignment is more reasonable.

The metal-thiocyanate linkage is "bent", and we might expect to see effects resulting from the lifting of the degeneracy of the π-donor orbital here. This orbital should split into bonding and non-bonding components, with the intense charge-transfer transition expected from the bonding component thus expected to shift to higher energy (relative to, say, the N-bonded isomer, where this π-orbital remains unsplit and does not participate very strongly in the bonding.) While the multitude of competing effects operating to shift charge-transfer energies does not allow very detailed analysis, the rather close similarity in the energy of charge-transfer (but not in intensity) for the N- and S-bonded isomers suggests that this splitting of the π-orbital is small.

An interesting additional case is the $Co(CN)_5NO_2^{3-}$ ion, which has previously been reported only as a product of kinetic studies.[53] We show the electronic spectrum of this ion in figure II-7. The shoulder at ~ 29 kK (345 nm) is assigned as the $^1A_1 \rightarrow {}^1E^a$ ligand-field band, its high energy being consistent with the high position of NO_2^- in the spectrochemical series. Following Fenske's assignments for the hexanitrometallates,[54] we assign the first charge transfer band in the pentacyano complex (at

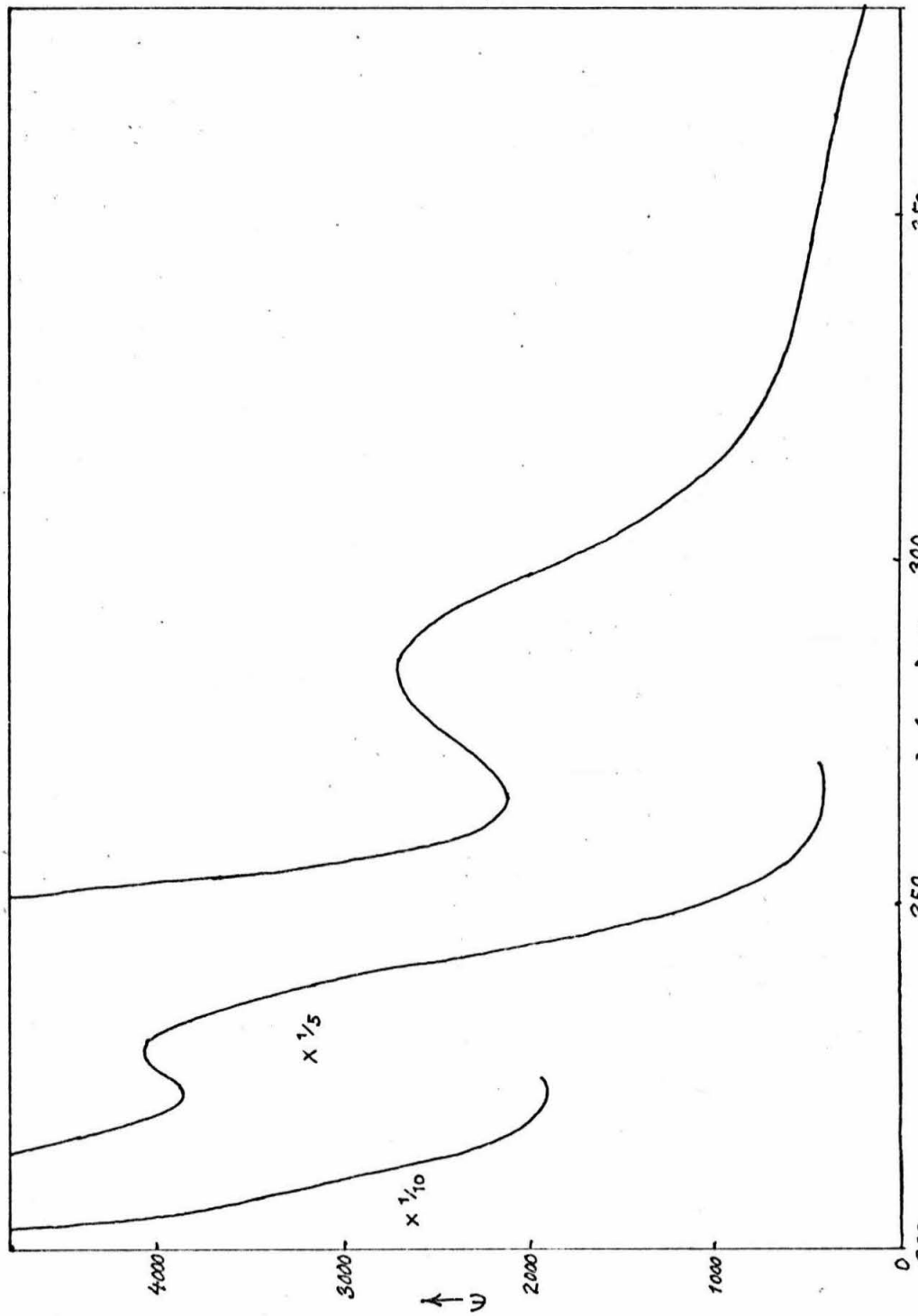


Figure II-7. Electronic spectrum of $K_3Co(CN)_5NO_2$ in aqueous solution, R.T.

35.2 kK) as a metal-to-ligand charge transfer transition (MLCT), while the transition at 43.6 kK is assigned as ligand-to-metal. In the C_{2v} symmetry of the complex (considering the symmetry of the ligand, and taking this as a weak perturbation on the C_{4v} symmetry of the metal ion environment) these transitions correspond to $^1A_1 \rightarrow {}^1A_1, {}^1B_2$ ($\{a_2 (d_{xy}), b_1 (d_{xz})\} \rightarrow b_1^* (NO_2^- \pi^*)$) for the MLCT, and $^1A_1 \rightarrow {}^1B_2$ (b_2 (NO_2^- π^{nb} orbital localized on oxygens) $\rightarrow$ $\{a_1 (d_{z^2}), a_1 (d_{x^2-y^2})\}$) for the LMCT. (Other possible transitions are not orbitally allowed or of higher energy.) We expect only small splitting of the d_{xy} and d_{xz} orbitals, hence only a single observable component of the metal-to-ligand charge transfer, while, because the ligand-to-metal charge transfer is shouldered on the cyanide charge transfer at higher energy, the observation of only a single component is not very distressing. (Actually, the $d\sigma^*$ splitting should also be rather small in this complex.)

The relative shift in energy of the two bands from those of the pentaammine[52] is of interest. The scatter in shifts for the various acidopentacyanide complexes, presumably reflecting a variety of different bonding interactions, is too large to make complex-to-complex comparisons viable. However, shifts of two bands in a single complex should still provide valid comparisons, especially in the case of the ligand-to-metal transition in this complex, which involves a primarily non-bonding orbital.

The shift of the MLCT transition (4.5 kK) is much larger than the shift of the LMCT transition (1.6 kK). This could be

interpreted as indicating a much greater π-acceptor capability of the NO_2^- b_1^* orbital in the cyano complex (increasing the energy of the b_1^* orbital), but we see no obvious rationale for this. We would preferentially interpret the shifts as reflecting the differences in interactions with metal orbitals of cyanide and ammine ligands. Our results would then indicate that the increased Δ of cyanide complexes results in large part from π-acceptor interactions with the $d\pi$ metal orbitals (which readily accounts for the increased energy of the MLCT transition). This interpretation of the cyanide ligand field would also provide further explanation of the decreased energy difference between ligand-field and charge-transfer transitions in the cyano complexes relative to ammine complexes. The validity of these conclusions is, of course, highly dependent on the correctness of the assignments of the charge transfer spectra of nitro complexes, a non-trivial problem.

Turning now to the charge transfer spectra of rhodium(III) and iridium(III) acidopentacyano complexes,[47] we observe very similar patterns, with transitions being shifted 7000 to 8000 cm^{-1} higher in energy for the rhodium complexes, and $\sim 13,000$ cm^{-1} higher for the iridium complexes. For $Rh(CN)_5SCN^{3-}$, we again observe two components of charge transfer, at 44.4 kK (ϵ = 18,000) and 49.5 kK (ϵ = 9,800), the splitting of 5.1 kK being consistent with our analysis of the transitions of the cobalt(III) complex.

In connection with our preceding discussion of charge-transfer transitions, we shall now consider the sulfito complexes $Co(CN)_5SO_3^{4-}$ and trans-$Co(CN)_4(SO_3)_2^{5-}$ whose photochemistry will be discussed in the section following this one. We have already presented the spectra of these complexes in figure II-4. When the spectra of these complexes were first considered, it was unclear whether the intense charge-transfer transitions at, respectively, 265 nm and 317 nm for the mono- and disulfito complexes, should be assigned as ligand-to-metal or metal-to-ligand, especially after consideration of the spectrum of the nitro complex. Our investigation of this problem is reported in detail, as the various correlations established are interesting.

In neutral or acidic solution, the disulfito complex rapidly aquates to the trans-sulfitoaquo complex, the spectrum of which is shown in figure II-8, along with that of the trans-sulfitohydroxo ion obtained in basic solution. The charge-transfer maximum in these ions is at almost identical energy to that of $Co(CN)_5SO_3^{4-}$.

The trans- and cis-tetraammine, bis(ethylenediamine), and bis(ammine)ethylenediamine cobalt(III) complexes, which have been reported by various workers[25,26] (primarily as useful synthetic intermediates), were also investigated. The spectrum of the trans-disulfito ions show an intense charge-transfer peak at ~325 nm, with a peak corresponding to the monosulfito ion growing in thermally at 275 nm in neutral or acidic solution. The spectra of substituted monosulfito derivatives[26] also show a peak at about

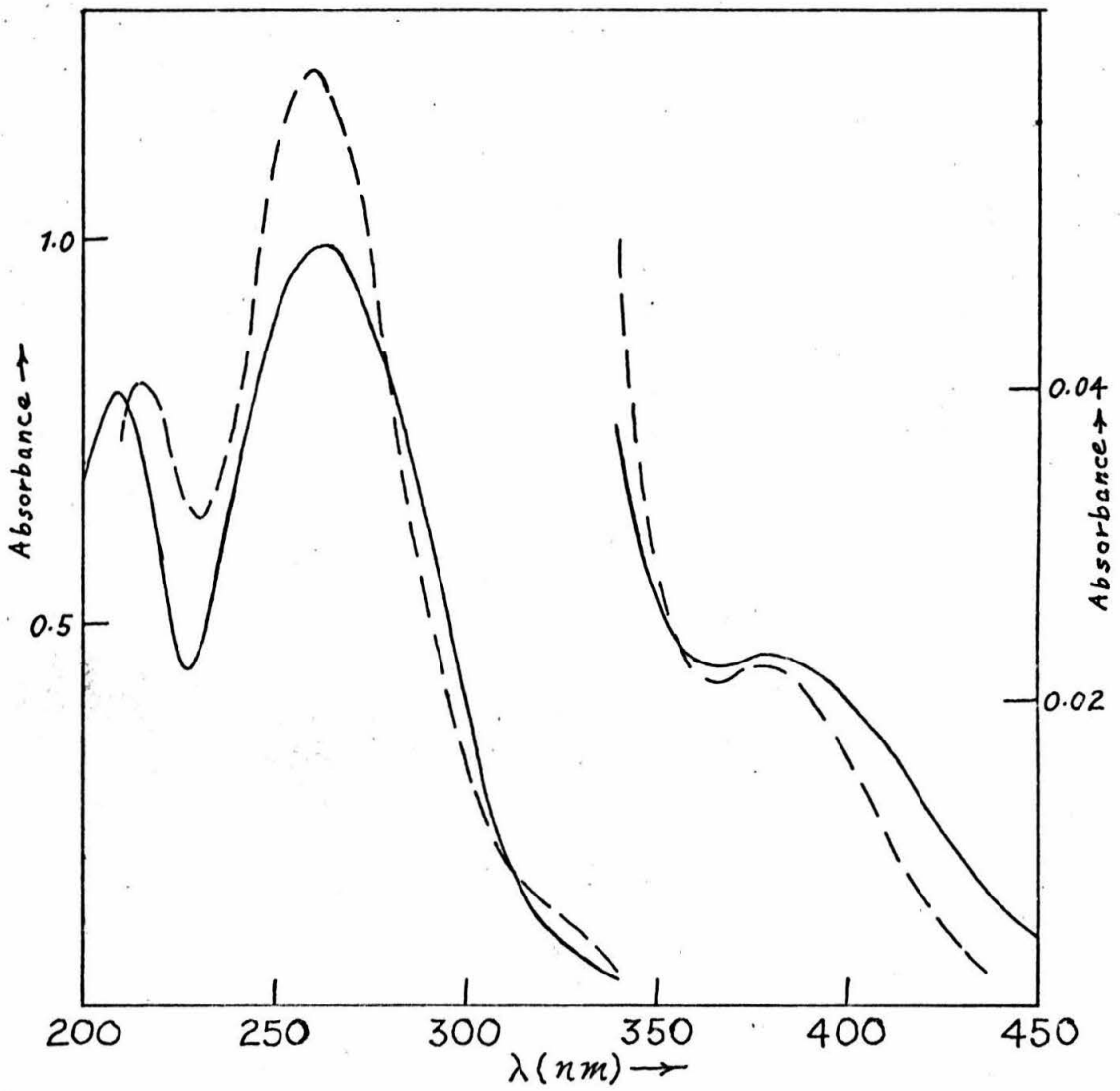


Figure II-8. Absorption spectra of 9.67×10^{-4} M trans-$Co(CN)_4(SO_3)(OH_2)^{3-}$ (——) and trans-$Co(CN)_4(SO_3)(OH)^{4-}$ (----).

this wavelength. The cis- derivatives, on the other hand, have a double peak, at approximately 300 nm and 260 nm, corresponding to the two allowed $\sigma \rightarrow M$ transitions expected in C_{2v} symmetry, and are rather thermally stable, probably equating with loss of ammines rather than sulfito groups. The correspondence of these spectra at least shows that the trans-disulfitotetracyano complex is indeed of trans-stereochemistry, while the small shifts to higher energy in the cyanide complexes are reminiscent of ligand-to-metal charge-transfer, as are the band patterns, which suggest excitation into the highly split "e_g" metal orbitals (particularly in order to explain the large shift to lower energy of the trans-disulfito derivatives relative to the monosulfito derivatives.)

The trans-disulfitotetraamminerhodium(III) ion[55] was also prepared, and was found to possess an intense C-T maximum at 262,5 nm, the mono-aquation product (produced either thermally or photochemically) having a maximum at 218 nm. The energy difference between the two peaks is 7.8 kK, comparing favorably to the value of 6.0 kK for the cobaltammine system and 6.5 kK for the cyanocobaltate system. The shift of 7500 cm^{-1} to higher energy between the rhodium and cobalt ammine complexes is again suggestive of ligand-to-metal charge transfer.

Finally, confirming a ligand-to-metal charge-transfer assignment, we prepared the $Fe(CN)_5SO_3^{5-}$ ion, whose spectrum is shown in figure II-9. The absence of low-energy charge-transfer

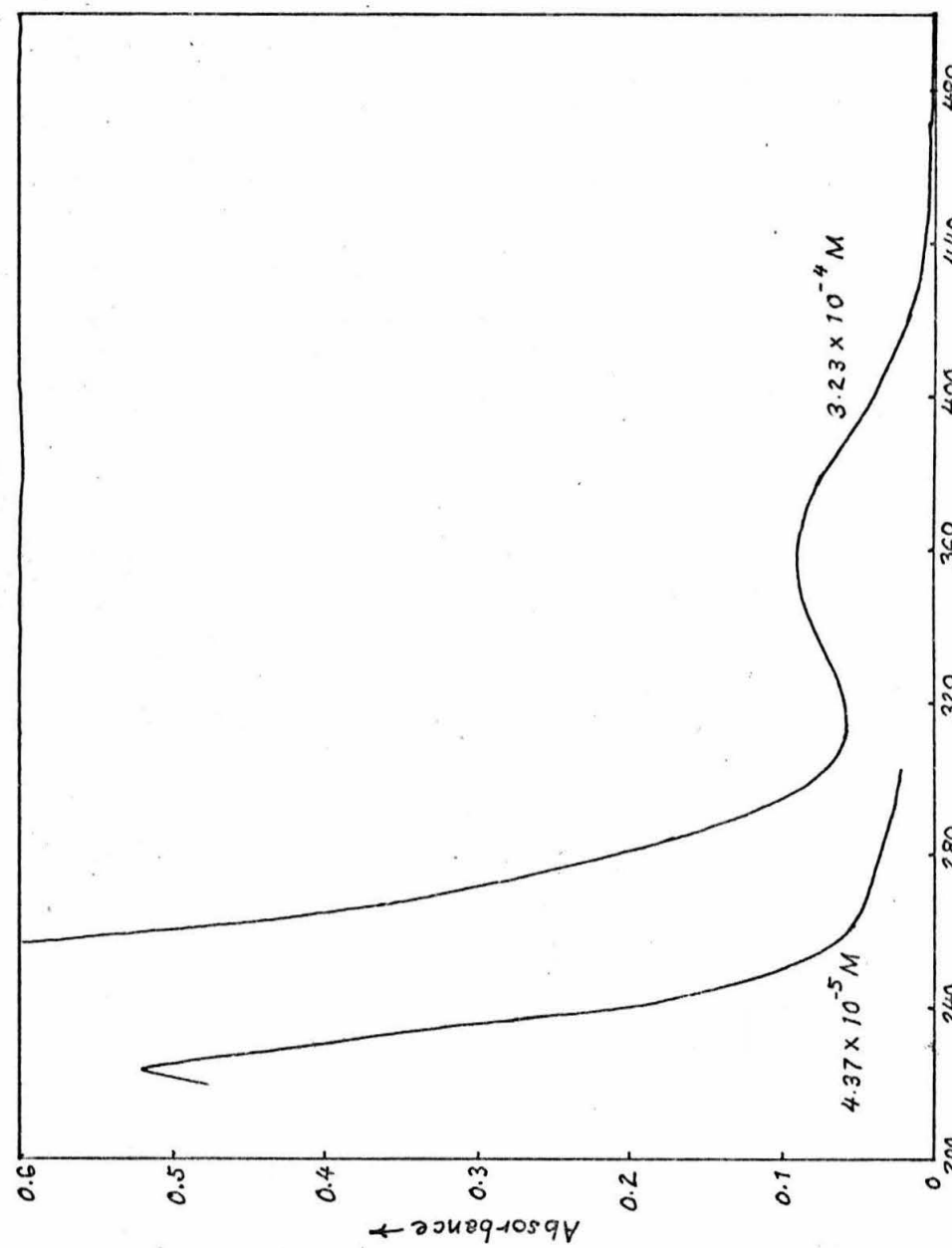


Figure II-9. Electronic spectrum of $Fe(CN)_5(SO_3)^{5-}$ in 2N NaOH, R.T.

maxima is consistent with a ligand-to-metal assignment, as metal-to-ligand transitions should shift to lower energy going from Co(III) to Fe(II) (both low-spin d^6), while ligand-to-metal transitions should shift in the opposite direction. The maximum at 224 nm is probably a cyanide MLCT transition rather than a sulfito charge-transfer band, as $Fe(CN)_6^{4-}$ has a cyanide CT band at 218 nm. The spectrum shown is in basic solution, resulting in a UV cutoff at ~ 220 nm. (In neutral buffered solution, $Fe(CN)_5SO_3^{5-}$ aquates rapidly, generating $Fe(CN)_5OH_2^{3-}$, whose $^1A_1 \rightarrow {}^1E^a$ maximum is at 495 nm, with maintenance of isosbestic points at 392 nm and 317 nm. In the UV region at neutral pH, $Fe(CN)_5SO_3^{5-}$ has a maximum at 217 nm, while thermal aquation gives a maximum at 197 nm with maintenance of isosbestic points at 207 nm and 190 nm.) It should also be mentioned that $Na_5[Fe(CN)_5SO_3] \cdot 9H_2O$ has an infrared spectrum, typical of S-bonded sulfito groups,[56] as do the cobalt complexes, thus eliminating any possible complications from linkage isomerism.

The ligand-to-metal sulfito charge-transfer bands may be assigned as $\sigma \rightarrow d\sigma^*$, both because of their high intensity, and because of the absence of a "$\pi \rightarrow d_{x^2-y^2}$" component in the spectra in figure II-4. We found the C-T spectra of the various substituted complexes to be extremely symptomatic of their stereochemistry, the two bands of the cis-complex, for example, easily distinguishing it from the trans- complex, while the shifts of the C-T band from mono-substituted to trans-disubstituted complexes are reminiscent of the behavior of the $^1A_1 \rightarrow {}^1E^a$ ligand field band. (In fact, the

the shift, ~6 kK, is almost numerically equal, as might be expected.)

Finally, we shall consider the cobalt-to-cyanide charge-transfer generally observed near 200 nm in the $Co(CN)_5X^{3-}$ complexes. The parent complex $Co(CN)_6^{3-}$ has this transition ($^1A_{1g} \rightarrow {}^1T_{1u}$) at 49.5 kK,[57] while all of the acidopentacyano-cobaltates have corresponding maxima at 49 to 51 kK. (See, for example, figure II-6.) The invariance in energy of this transition is again indicative of only a small splitting of the "t_{2g}" metal orbitals in a C_{4v} ligand field. (Considering the large variation in the energy of the d_{z^2} orbital in the various complexes, this approximate energy invariance is rather convincing proof that the transition is indeed an MLCT transition.) The apparent intensity of this transition is subject to considerable variation, the peak ϵ decreasing from 35,000 for the hexacyanide to 12,000 for $Co(CN)_5Br^{3-}$. The peak is also observed to broaden, and splitting (of the expected order of 1000 cm^{-1}) into the allowed $^1A_1 \rightarrow {}^1E$ (b_2 (d_{xy}) e (π^*CN)) and $^1A_1 \rightarrow {}^1A_1$ (e^3 ($d_{xz, yz}$) e (π^*CN)) transitions might account for this.

Photochemistry

The photochemical reactivity of cyanocobaltate complexes has been investigated by many workers.[41,59] Surprisingly, the only reaction which has been reported is photoaquation via a dissociative-type mechanism, which seems strictly analogous to the thermal chemistry. Neither photoredox reactions nor

substitution of cyanide (except in the hexacyanide) has been reported. (The only reported exception to the dissociative mechanism is the hexacyanide,[58] whose photoaquation proceeds via an interchange mechanism, with a non-scavengable intermediate.)

This situation is in marked contrast to the photochemistry of cobaltammines, which includes prominent photoredox reactions.[59] It is reasonable to speculate that this difference in behavior arises from factors related to the much greater kinetic stability of $Co(CN)_5^{3-}$ relative to $Co(NH_3)_5^{2+}$.[60] Certainly as far as vertical excitation energies are concerned, the charge-transfer states in the cyanide complexes are nearer in energy to the ligand field states than they are in the ammines, and although we can probably expect the energies of the "relaxed" (thermally equilibrated) C-T states to be less than the spectroscopic energies in both cases, we can also expect this effect to be comparable in the cyanides and ammines. What we do not know is how dissociative the C-T states are, and if ground state properties are relevant, then we certainly expect the cyanide C-T states to have less tendency to "fall apart."

In any case, the lack of photoredox behavior observed is chemically convenient, and allows simple mechanistic inferences to be made as to excited state reaction pathways, via identification of the kinetically inert Co(III) products. Unfortunately for such investigations in the past, the photochemistry of the complexes

seemed identical to (and perhaps even was) that of a "hot" ground state. (A recent study showing that biacetyl triplets are quenched by the (presumably lowest) excited state of a variety of $Co(CN)_5X^{3-}$ complexes has at least implicated a triplet state, or perhaps a quintet state, vide infra, as an intermediate in the reaction pathway.)

However, the invariant reactivity patterns of $Co(CN)_5X^{3-}$ complexes remained a hindrance towards elucidation of the reactive states and internal energy conversion mechanisms. We decided to investigate the photochemistry of trans-$Co(CN)_4(SO_3)_2^{5}$ and its various derivatives, in hopes of finding more varied reaction paths, and were rewarded with a variety of photochemical reaction paths which were quite different from the thermal chemistry (which consisted of aquation of one, and only one, sulfito group). As an addition bonus, techniques and insights obtained in this study have allowed us to find similar reaction paths in the photochemistry of some $Co(CN)_5X^{3-}$ complexes. All of the work described in this section was done in collaboration with Dr. Mark Wrighton.

Reactions I-5 have been observed upon irradiation of aqueous solutions of the sulfito complexes. Figure II-10 shows a typical plot of the decay of the C-T absorption of trans-$Co(CN)_4(SO_3)_2^{5-}$ upon 366 nm irradiation in alkaline medium. The disappearance quantum yields for the complexes are summarized in table II-3 for several irradiation wave lengths. Reactions 1) and 2) were studied at pH = 13, thereby precluding the possibility of protonated complexes.

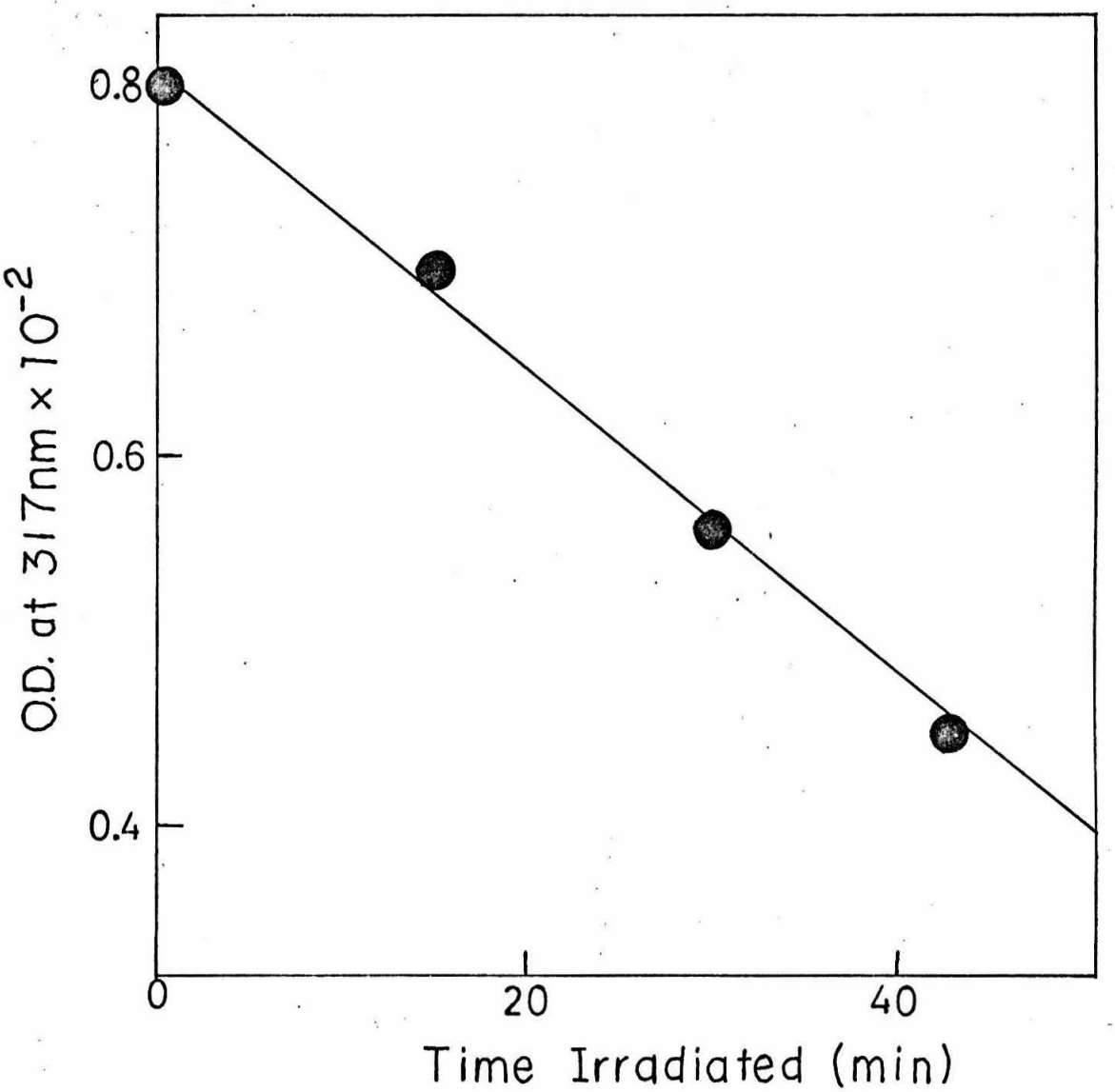


Figure II-10. Decay of 317 nm absorption upon 366 nm irradiation of <u>trans</u>-$Co(CN)_4(SO_3)_2^{5-}$ in 0.1 <u>M</u> NaOH. Light intensity is 1.28×10^{-7} ein/min.

Table II-3

Disappearance Quantum Yields[a] for

$K_n Co(CN)_4(SO_3)(X)$ Complexes

Compound	pH	$\Phi_{254\ nm}$	$\Phi_{313\ nm}$	$\Phi_{366\ nm}$	$\Phi_{436\ nm}$
$K_5Co(CN)_4(SO_3)_2$	>13	--	0.36	0.57	0.57
$K_3Co(CN)_4(SO_3)(OH_2)$	~ 2	0.15	0.11	0.14	--
$K_4Co(CN)_4(SO_3)(OH)$	>13	0.13	0.09	0.19	--
$K_4Co(CN)_5SO_3$	7	0.25	--	--	--

[a]Quantum yields are ± 10%.

1) $\underline{\text{trans}}\text{-}Co(CN)_4(SO_3)_2^{5-} \xrightarrow[OH^-]{h\nu} \underline{\text{trans}}\text{-}Co(CN)_4(SO_3)(OH)^{4-} + SO_3^{2-}$

2) $\underline{\text{trans}}\text{-}Co(CN)_4(SO_3)(OH)^{4-} \xrightarrow[OH^-]{h\nu} Co(CN)_4(OH)_2^{3-} + SO_3^{2-}$

3) $\underline{\text{trans}}\text{-}Co(CN)_4(SO_3)(OH_2)^{3-} \xrightarrow[OH^-]{h\nu} Co(CN)_4(OH_2)_2^{-} + SO_3^{2-}$

4) $\underline{\text{trans}}\text{-}Co(CN)_4(SO_3)(OH_2)^{3-} \xrightarrow{254\ nm}$ decomposition to Co(II)

5) $Co(CN)_5(SO_3)^{4-} \xrightarrow[H_2O]{h\nu} Co(CN)_5(OH_2)^{2-} + SO_3^{2-}$

The principal photoproduct from the disulfito complex is $\underline{\text{trans}}\text{-}Co(CN)_4(SO_3)(OH)^{4-}$, as evidenced by the onset of the characteristic C-T band at 260 nm. The loss of sulfite from the monosulfito complexes on further irradiation is established by the disappearance of low-energy C-T absorption. Addition of 0.5 M Na_2SO_3 to neutral solutions of the diaquo complex results in nearly quantitative regeneration of the initial $\underline{\text{trans}}\text{-}Co(CN)_4(SO_3)_2^{5-}$, strongly supporting the assignment of the product as $Co(CN)_4(OH_2)_2^{-}$ in neutral or acidic solution, and as the dihydroxo complex in basic solution. (A similar product can be formed in solution when nitric acid[62] or hydrogen peroxide is used to oxidize the sulfito groups. Solid salts are not isolable, insoluble yellow (presumably polymeric) material being obtained.) The spectrum in the ligand field region, shown in figure II-11 for the dihydroxo complex, seems most consistent with a cis-stereochemistry, but may well represent a trans-, cis- mixture, considering the lability implied by its extremely rapid back-reaction with sulfite. The sulfito-aquo complexes are also thought to undergo trans- to cis- isomerization,

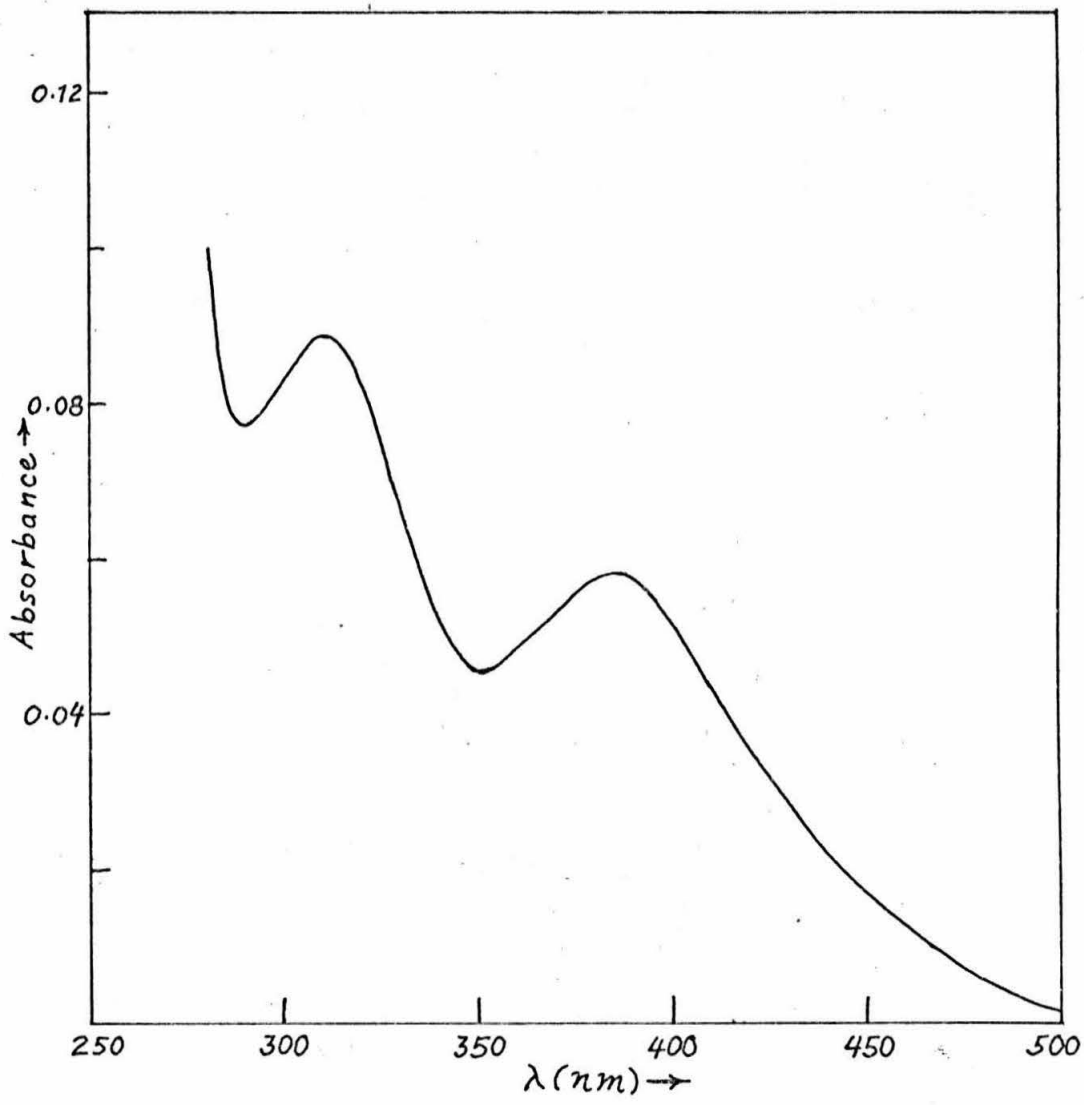


Figure II-11. Absorption spectrum of photolysis product of trans-$Co(CN)_4(SO_3)OH^{4-}$ in 0.1 M NaOH.

at a relatively slow rate.[63] Our previous comments on the stability of $Co(CN)_5OH_2^{2-}$ are relevant here, as is the fact that cis- and trans-$Co(NH_3)_4(OH)_2^{3+}$ are known to be in relatively labile equilibrium in solution, particularly at basic pH's, and also facilely form a tetramer.[64]

We investigated the photochemistry of $Co(CN)_4en^-$, in an effort to produce a "cis"-diaquo product, but found that, even in acidic solution, which should have aided in preventing recoordination of half-dissociated ethylenediamines, quantum yields for production of diaquo complexes were very low, and photo-reduction of the product (vide infra) was competitive with the initial photolysis. (Intermediate rise in absorption near 380 nm was noted, and we suspect that the product was the same as that in the photolysis of the sulfito complexes.)

The formation of Co(II) has been established as a primary reaction, reaction 4). Figure II-12 shows the build-up of Co(II) and the disappearance of trans-$Co(CN)_4(SO_3)(OH_2)^{3-}$ upon 254 nm irradiation. The quantum yield for Co(II) production is 0.01, to be compared to the quantum yield of 0.15 for the disappearance of parent complex. Reduction is thus a minor pathway. The modest yields of Co(II), along with possible polymerization of the diaquo complex, account for the observation that trans-$Co(CN)_4(SO_3)_2^{5-}$ cannot be completely regenerated upon addition of SO_3^{2-} to completely reacted mixtures. As implied by the steady rise of

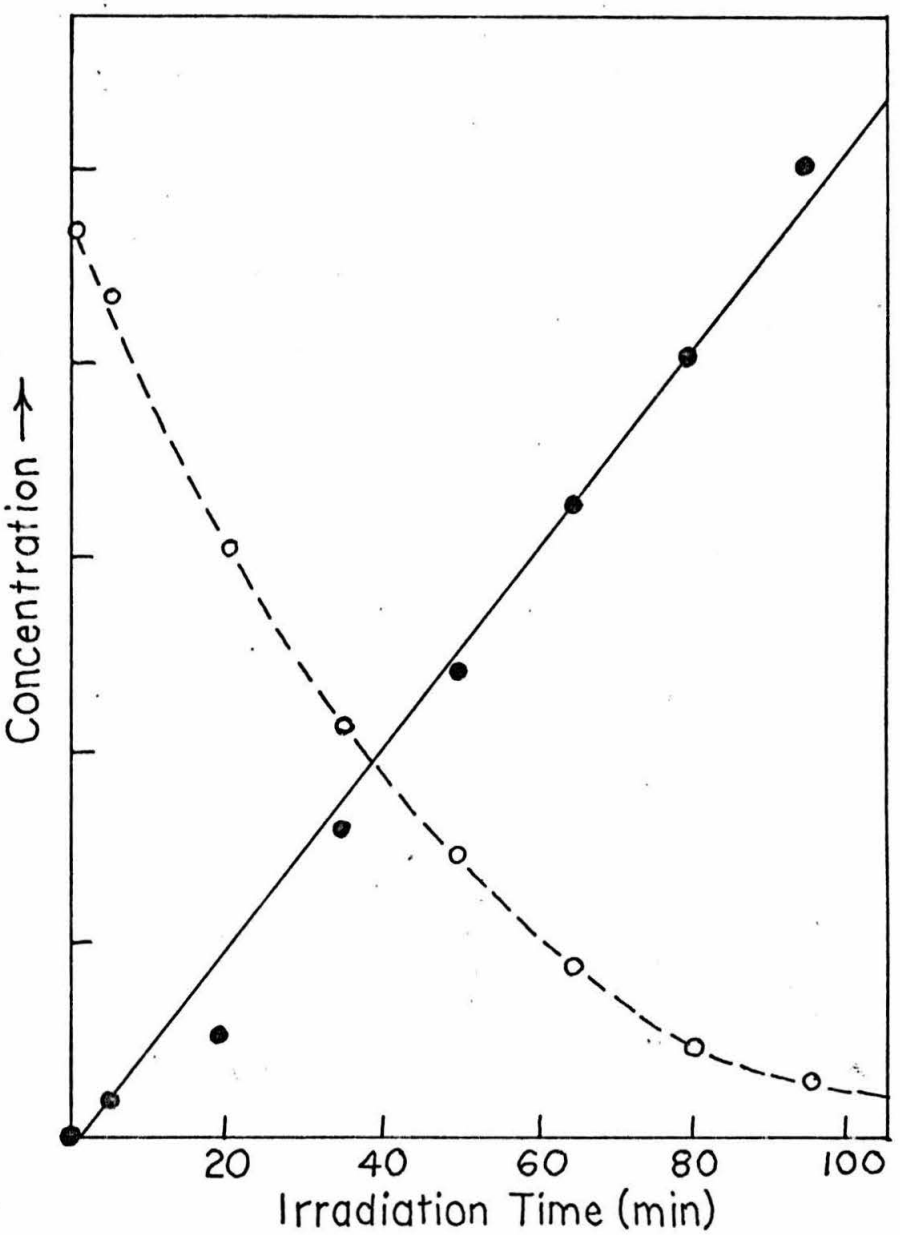


Figure II-12. Disappearance of trans-$Co(CN)_4(SO_3)(OH_2)^{3-}$ (○) and appearance of Co(II) (●) upon 254 nm photolysis in 0.01 M $HClO_4$. The concentration scales are not the same.

Co(II) concentration at long irradiation times, Co(II) is also a product of "diaquo" photolysis.

In table II-4 we report the effect of added SO_3^{2-} on the disappearance rates of the trans-$Co(CN)_4(SO_3)_2^{5-}$ complex. Addition of 1.4 M $NaClO_4$ had no effect on the rate of photodisappearance, indicating no ionic strength dependence.

Mechanistic discussion for the observed photoreactions must account for the wavelength dependent quantum yields, the specific loss of the sulfito group, the photoreduction to yield Co(II), and the repression of the initial rate of photodisappearance of $Co(CN)_4(SO_3)_2^{5-}$ upon addition of Na_2SO_3. It is attractive to assume that Co(II) is only formed by population of CT excited states. The reduction Co(III) → Co(II) is consistent with the SO_3^{2-} → Co(III) CT band assignment. The CT states could also lead to photosubstitution by a mechanism similar to that proposed for $Co(NH_3)_5(X)^{n+}$ complexes.[59] Substitution via a CT excited state should yield preferential loss of the sulfito group since the primary step would be homolytic cleavage of the Co-SO_3 bond. Invoking the CT excited state adequately accounts for the increase in quantum efficiency upon 254 nm excitation relative to 313 nm irradiation for the aquo and hydroxo complexes.

In contrast to the CT excited states, ligand field excited states are thought to yield only substitution chemistry.[59] Upon irradiation at 366 nm or 436 nm the sulfito complexes undergo the d_{xz}, d_{yz} → d_{z^2} ($^1A_1$ → ^1E) transition, which should selectively

Table II-4

Quenching of Photosubstitution of $trans\text{-}Co(CN)_4(SO_3)_2^{5-}$ with SO_3^{2-} [a]

Added Reagent	Concentration, M	Relative Rate
None	--	1.00
SO_3^{2-}	0.2	0.6_1
SO_3^{2-}	0.4	0.03_6
SO_3^{2-}	1.0	0.2_5
$NaClO_4$	1.4	$1._0$

[a] Irradiation source was a 75W Pyrex filtered Hg lamp.

labilize ligands on the z axis of the molecule assuming the d_{z^2} and $d_{x^2-y^2}$ levels are separated enough to insure a "localized" $d_{z^2}\sigma^*$ excitation. The one-electron population of the d_{z^2} orbital substantially weakens the metal-ligand bonds on the z axis. Further, the depopulation of the d_{xz}, d_{yz} orbitals affects the axial π-bonding; for π-acceptor ligands depopulation of d_{xz}, d_{yz} leads to greater lability while some relative kinetic stability is gained for π-donor ligands. The H_2O ligand is recognized as a σ-donor only, whereas OH^- is characterized as a π-donor ligand. The sulfur donor $-SO_3^{2-}$ is classed as a π-acceptor ligand based on its high position in the spectrochemical series and its strong trans labilizing power in cyanocobaltate(III) complexes.[23,63] The most significant reaction associated with ligand field excitation is the loss of sulfite, consistent with the prediction of a greatly weakened Co(III)-SO_3 bond upon depopulation of π-bonding orbitals (d_{xz}, d_{yz}) and population of $d_{z^2}\sigma^*$. In the ground state loss of sulfite from either the aquo or hydroxo complex does not occur except under vigorous conditions. Unfortunately, the rapid rate of thermal loss of H_2O in trans-$Co(CN)_4(SO_3)(OH_2)^{3-}$ precludes the measurement of the rate of excited state H_2O substitution. For the σ-donor H_2O, though, the excited state substitution rate should be faster than the ground state rate. If we assume that all of the substitution processes occurring from ligand field excited states are dissociative, as suggested by the rate data in the presence of varying amounts of Na_2SO_3, then it is probable that one photon

results only in the substitution of one molecule of H_2O, since the five-coordinate intermediate is not likely to be in an electronically excited state. The H_2O exchange quantum yield, then, must be less than 0.90 since loss of SO_3^{2-} has greater than 0.1 quantum efficiency. This leads to the conclusion that the labilizing effect of electronic excitation is much greater for the sulfito than for the aquo group.

The relative degree of labilization of the OH^- and SO_3^{2-} ligands in trans-$Co(CN)_4(SO_3)(OH)^{4-}$ is predicted to differ even more. Since OH^- is a π-donor ligand the effect of one-electron population of the $d_{z^2}\sigma^*$ is partially compensated by the depopulation of the d_{xz}, d_{yz} orbitals. The rate of OH^- substitution, then, will not undergo as large a change as for the σ-donor H_2O.

The general decrease in reaction quantum yields upon 313 nm irradiation implicates a third excited state which gives less efficient reaction and/or incomplete internal conversion to the lower lying excited states. Nonradiative decay from this state must occur directly to the ground state. We suggest that this state is the $^1A_2$ state, which arises from the purely equatorial $d_{xy} \rightarrow d_{x^2-y^2}$ excitation. The $^1A_2$ state does not mix with the lower energy states of E symmetry.

As with the $Co(CN)_5(X)^{n-}$ complexes, the ligand field excited state substitution reaction apparently proceeds primarily via a dissociative mechanism since added SO_3^{2-} suppresses the rate of sulfite substitution. The five-coordinate species produced

via photolysis of trans-$Co(CN)_4(SO_3)_2^{5-}$ may be the same as that produced in the thermal dissociation.[23] It is interesting that the photosubstitution is very efficient in strongly alkaline media even though the thermal reaction is apparently acid catalyzed.[23]

We have used the rapid thermal reaction of sulfite with $Co(CN)_4(OH_2)_2^-$ as a probe for production of this ion in other systems, the intense transition at 317 nm allowing simple determination of disubstituted products, and find small but real quantum yields (of the order of 0.01 to 0.05) for disubstituted products of $Co(CN)_5X^{3-}$ when X^- is a π-donor. On the other hand, $Co(CN)_5(SO_3)^{4-}$, SO_3^{2-} being a strong π-acceptor, gives no disubstituted products. We thus find that the photochemistry of $Co(CN)_5X^{3-}$ is not, in fact, cleanly photosubstitution of X^-, and that other reaction paths are possible, the relative efficiency of the various paths being understandable in terms of the bonding modes of the various ligands. A detailed model of the photochemical reactions of metal complexes, based on elaboration of these ideas, has recently been developed.[65] Such a model is, of course, limited by the validity of the descriptions of the excited states that one uses in it. While the work described in this chapter provides some characterization of the nature and relative energies of the various excited states, the simple question of the lowest excited state is still open, surprisingly. Emission is observed from $Co(CN)_6^{3-}$ (very weak, with no emission having yet been reported for any $Co(CN)_5X^{3-}$ complex) at 14.4 kK,[66] greatly red-shifted from the first singlet

d-d band at 31.05 kK. The energy of the emission seems quite inconsistent with triplet emission, and the possibility of this being quintet emission presents itself. Although the vertical energy of the lowest quintet state is quite high, symmetrical expansion of all metal-cyanide bands must eventually lead to the quintet actually passing below the ground-state potential surface at some value of the internuclear distance (as such expansion leads to a decrease of Δ.) The "relaxed" quintet state may have a quite large value of the internuclear distance, and conceivably, it might cross the lowest triplet state (also relaxed) at accessible vibrational levels of the triplet, further relaxing to give very low energy emission. This argument is probably not relevent to the "axially localized" low-lying excited states of $Co(CN)_5X^{3-}$ complexes, for which we expect primarily Co-X bond stretching rather than symmetrical expansion, resulting in the quintet state being less easily accessible. This may account for both the lack of observable emission in these complexes (the triplet conceivably showing efficient vibrational deactivation to the ground state) and the different mechanisms for substitution. (We mentioned earlier the non-dissociative mechanism prevailing for $Co(CN)_6^{3-}$.)

Thus, we are still far from a complete description of the excited state manifold of even as simple and well-studied a metal ion as Co(III). Needless to say, "further studies are planned."

However, the stated purpose of our present work, which was to provide a consistent description of the absorption spectra of the complexes, has been accomplished.

CHAPTER III

Phosphine Complexes of d^6 Metal Ions

Introduction

In the course of studies of the dioxygen complexes to be discussed in Chapter V, we became interested in the spectra of metal complexes of the bidentate, chelating arylphosphine ligands 1,2-bis(diphenylphosphino)ethane, abbreviated as 2-phos, and cis-1,2-bis(diphenylphosphino)ethylene, abbreviated as 2=phos. (These ligands have been given many different trivial names in the literature. We use those of Vaska, et al.[163] as they emphasize the structure similarities of the ligands.)

The electronic structures of phosphine (and arsine) metal complexes are still somewhat ill-understood. Extensive studies[68,69] of 5-coordinate complexes of (primarily) d^8 metal ions have at least established that certain low-energy bands observed are ligand-field bands, in spite of their extremely high intensities. However, such studies have given a limited view of the potentially unusual bonding interactions of phosphine ligands, characterizing them at best by an estimate of the position of phosphine ligands in the spectrochemical series. The rich charge-transfer spectra of the complexes have also been relatively neglected, one attempt[69] to characterize them having been hampered by the low symmetry of most of the complexes considered, as well as by extreme uncertainty as to the energy

of ligand-to-metal charge-transfer transitions involving other ligands in the complexes.

We have prepared a number of complexes of the formula trans-$Co(2\text{=}phos)_2X_2^+$, and have attempted to analyze their spectra by analogy to those of other, well-understood Co(III) complexes. Low-energy charge-transfer absorption due to the predominant ligand in these complexes is a complication not encountered in ammine and cyanide complexes of Co(III), and the charge-transfer spectra are extremely complex. In order to aid in their interpretation, we have reinvestigated a number of carefully chosen d^8 metal complexes.

We have also investigated the spectra of the free phosphine ligands, to gain insight into their electronic structure, and also so as to be able to distinguish ligand absorption in metal complexes.

Experimental

Preparation of Compounds

The complexes $Ni(2\text{-}phos)X_2$ (X = Cl, Br) were prepared by the method of Van Hecke and Horrocks.[70]

$Ni(2\text{=}phos)Cl_2$ and $Ni(2\text{=}phos)_2Cl_2$ were prepared by the method of Meek and McAuliffe.[71] $[Ni(2\text{-}phos)_2](ClO_4)_2$ was prepared by the slow addition of a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ in ethanol to a boiling solution of the stoichiometric quantity of 2-phos in ethanol. A finely crystalline yellow solid formed immediately. (Preparation of this complex has also been reported by Nyholm, et al.[72])

The complexes $Co(2\text{-phos})_2X_2$ (X = Cl, Br) were prepared by the method of Horrocks, et al.[73] $Co(2\text{=phos})_2X_2$ (X = Cl, Br, I) were prepared by appropriate modification of this procedure.

trans-$[Co(2\text{=phos})_2Cl_2]ClO_4$. Chlorine gas was bubbled rapidly through a solution of $Co(2\text{=phos})_2Cl_2$ (0.5 g) in 25 ml of CH_2Cl_2. A green solid began to form almost immediately. After 15 minutes, nitrogen was bubbled briefly through the solution to remove excess chlorine. The product was filtered off and washed with a small amount of cold CH_2Cl_2, and then thoroughly washed with ether. This chloride salt was dissolved in absolute ethanol and a few drops of saturated ethanolic $NaClO_4$ added. Storage at 0 °C overnight gave green crystals of the perchlorate salt, which were filtered off and washed with cold ethanol and ether.

Analysis:

Calcd. for $[Co(2\text{=phos})_2Cl_2]ClO_4$: C, 60.9; H, 4.79; Cl, 10.4; P, 12.1; Co, 5.7.

Found: C, 59.2; H, 4.64; Cl, 10.9; P, 8.7; Co, 6.9.

On one occasion, the initial reaction solution was allowed to stand (stoppered) for ~2 weeks. The precipitate of the chloride salt slowly redissolved and very large dark green crystals of the tetrachlorocobaltate salt formed on standing. The crystals were filtered off and washed thoroughly with water to remove a pink contaminant (presumably $CoCl_2 \cdot 6H_2O$) and finally washed with ether. Analysis indicates that the salt crystallizes with three solvent molecules per formula unit.

Analysis:

Calcd. for $[Co(2=phos)_2Cl_2]_2[CoCl_4] \cdot 3CH_2Cl_2$: C, 55.66; H, 4.45; Cl, 21.50; P, 10.73; Co, 7.66.

Found: C, 53.81; H, 4.22; Cl, 21.86; P, 10.47; Co, 7.54.

The trans-$Co(2=phos)_2Cl_2^+$ ion could also be prepared from $Co(2=phos)_2O_2^+$.[163] A few drops of concentrated hydrochloric acid were added to a concentrated methanol solution of $[Co(2=phos)_2O_2]ClO_4$, with no immediate reaction resulting. On standing overnight, green crystals of the product (as the chloride salt) formed. They were identified by their electronic spectrum.

trans-$[Co(2=phos)_2Br_2]ClO_4$ was prepared by a procedure analogous to that employed for the trans-dichloride. The stoichiometric amount of liquid Br_2 was added to a CH_2Cl_2 solution of $Co(2=phos)_2Br_2$ and the brown solid product filtered off. Recrystallization from ethanol with $NaClO_4$ gave orange-brown crystals of the perchlorate salt.

Analysis:

Calcd. for $[Co(2=phos)_2Br_2]ClO_4$: C, 56.01; H, 4.34; P, 11.11; Br, 14.33; Cl, 3.18; Co, 5.29.

Found: C, 53.71; H, 4.23; P, 10.23; Br, 13.51; Cl, 5.19; Co, 5.54.

trans-$[Co(2=phos)_2I_2]I$ could be obtained by an analogous method as shiny brown-black crystals. It was not further investigated.

trans-$[Co(2=phos)_2(CNS)_2]ClO_4$. A large excess of NaSCN was refluxed with trans-$[Co(2=phos)_2Cl_2]ClO_4$ in methanol for one hour. Addition of a large excess of saturated methanolic $NaClO_4$ gave a brownish-yellow precipitate. This precipitate was again refluxed with excess NaSCN in methanol, reprecipitated, washed thoroughly with water, dissolved in ethanol, and crystallized slowly by addition of a few drops of saturated ethanolic $NaClO_4$ and cooling overnight at 0 °C. The product formed as shiny brown, blunt needles.

trans-$Fe(2=phos)_2Cl_2$ was prepared by mixing filtered solutions of the stoichiometric amounts of $FeCl_2 \cdot 6H_2O$ and the ligand in methanol under nitrogen and refluxing. Cooling gave yellow crystals of the product.

trans-$[Rh(2=phos)_2Cl_2]ClO_4$. 1.5 g of solid 2=phos was added slowly to a boiling solution of 0.4 g of $RhCl_3 \cdot 3H_2O$ in 25 ml of absolute ethanol. The solution lightened and a yellow precipitate formed rapidly. The solution was cooled and ether added to complete precipitation. The product was filtered off and dissolved in boiling ethanol, and saturated ethanolic $NaClO_4$ added dropwise. The complex precipitated as a bright yellow powder. (The rhodium(I) complex $Rh(2=phos)_2^+$, both as its chloride and perchlorate salts, is much more soluble in ethanol than the rhodium(III) complex, and any contamination is removed at this stage.)

Analysis:

Calcd. for $[Rh(2\text{-phos})_2Cl_2]ClO_4$: C, 58.37; H, 4.52; Cl, 9.94; P, 11.56; Rh, 9.62.

Found: C, 57.1; H, 4.52; Cl, 10.3; P, 11.5; Rh, 8.8.

The above complex was also prepared as the pure Cl^-, $B(C_6H_5)_4^-$ and PF_6^- salts by precipitation from alcoholic solution with an excess of the appropriate anion.

trans-$[Rh(2\text{-phos})_2Cl_2]Cl \cdot 3C_2H_5OH$. The crude chloride salt of this complex was obtained as for the 2-phos complex. This was dissolved in boiling ethanol, ether was added, and the solution was cooled. The resulting large, well-formed, yellow crystals were filtered off and washed with ethanol and ether. The infrared spectrum of this compound indicates the presence of ethanol of crystallization, and the analytical results suggest 3 ethanols per formula unit.

Analysis:

Calcd. for $[Rh(2\text{-phos})_2Cl_2]Cl \cdot 3C_5H_5OH$: C, 60.8; H, 5.81; Cl, 9.3; P, 10.8; Rh, 8.9.

Found: C, 60.8; H, 5.69; Cl, 9.4; P, 11.1; Rh, 8.4.

Physical Measurements

Spectral measurements were done as described in Chapter II. The compounds described in this chapter are water-insoluble, and low-temperature measurements were done in commercial EPA solvent. As the compounds were nearly insoluble in pure EPA,

they were generally dissolved in some "good" solvent, such as CH_2Cl_2 or acetonitrile, and diluted with EPA. As long as the resulting solvent was at least 6:1 EPA, it had good glass characteristics at liquid nitrogen temperature. The solvent was found to contract by 22% at 77°K.

The spectra of complexes in the solid state were measured for finely ground Nujol mulls of the compounds pressed between optical quality quartz plates.

Emission spectra and excitation spectra were measured on a Perkin Elmer-Hitachi MPS-3 fluorescence spectrophotometer employing the spectral correction accessory supplied with the instrument.

Results and Discussion

Phosphine Ligands

In figure III-1, we show the electronic spectrum of 2-phos in acetonitrile, which is similar to the spectrum of most aryl phosphines. (The spectrum of 2-phos is quite similar, both in band positions and intensities.) The broad, intense peak at 256 nm (ϵ = 21,000) is at about the same energy as the first singlet $\pi \rightarrow \pi^*$ transition of benzene, but cannot be assigned as a phenyl transition because of its large intensity and large blue-shift with increasing solvent polarity, both features being characteristic of $n \rightarrow \pi^*$ transitions.

The comparison between triphenyl phosphine and triphenyl phosphine oxide is instructive, triphenyl phosphine showing[74] a broad band at 261 nm ($\epsilon \simeq$ 11,000) in methanol, with the oxide[74]

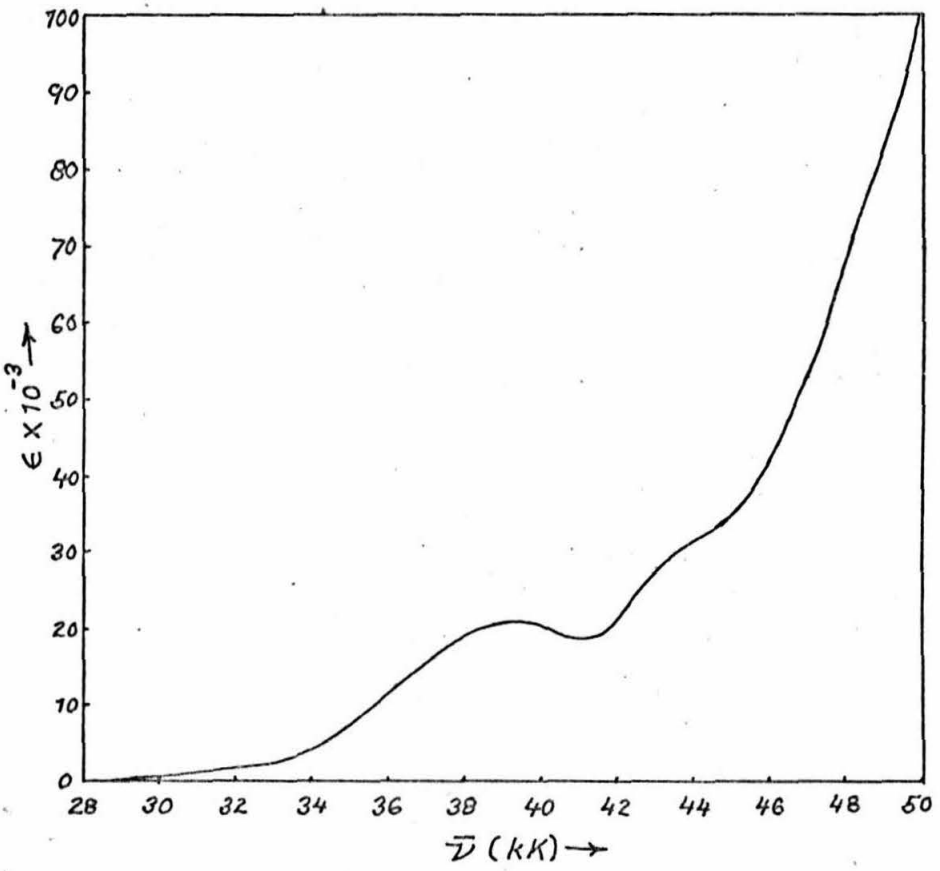


Figure III-1. Electronic spectrum of cis-bis(diphenylphosphino)ethylene (2=phos) in acetonitrile, R.T.

having at the same energy a sharply vibrationally structured band, with $\epsilon = 1960$ for the most intense spike. The latter spectrum is fairly typical of substituted benzenes, the band being readily assignable to a $\pi \rightarrow \pi^*$ transition, red-shifted and intensified relative to that of benzene at 256 nm, $\epsilon = 204$.[75]

Compounds such as $C_6H_5As(CF_3)_2$ show a strongly blue-shifted $n \rightarrow \pi^*$ transition (because of stabilization of the hetero-atom lone pair by the electron-withdrawing trifluoromethyl groups) and a relatively weak $\pi \rightarrow \pi^*$ transition may be observed on the low-energy side of the $n \rightarrow \pi^*$ transition.[76] We can thus infer that in other aryl phosphines, arsines, and stibenes a weak $\pi \rightarrow \pi^*$ transition underlies the $n \rightarrow \pi^*$ transition, eliminating any ambiguity as to the identity of this peak. We thus assign the peak at 256 nm in the spectrum of 2-phos as $n \rightarrow \pi^*$.

The shoulder at ~ 230 nm ($\epsilon \simeq 29,000$) may be assigned as the second expected $\pi \rightarrow \pi^*$ transition, which is seen at 223 nm ($\epsilon \simeq 21,000$) in the spectrum of triphenyl phosphine oxide.[79] This transition is also, as expected, red-shifted from the benzene transition at 200 nm ($\epsilon = 7,400$).[75] In a large number of mono-substituted benzenes, the ratio of the wavelengths of the first and second $\pi \rightarrow \pi^*$ transitions has been shown to be constant[77] and we can therefore estimate the wavelength of the lowest $\pi \rightarrow \pi^*$ transition to be ~ 280 nm. The observed $n \rightarrow \pi^*$ transition is, actually, rather unsymmetric toward lower energy, and a $\pi \rightarrow \pi^*$ transition here seems reasonable. Preer[69] observed weak vibrational structure

between 35 and 38 kK in low temperature spectra of aryl arsines, which is completely consistent. The wavelengths of the $\pi \rightarrow \pi^*$ transitions indicate the aryl phosphine to be comparable to aniline, as far as the electronic structure of the phenyl groups is concerned, which is also quite reasonable. (This incidentally indicates a rather large degree of "conjugation" of the phosphorus lone pair electrons with the phenyl groups.)

A poorly defined shoulder is observed at ~ 206 nm, $\epsilon \simeq 70,000$, which might be assigned to the expected allowed phenyl $\pi \rightarrow \pi^*$ transition, or to any of a number of other possible transitions.

We can expect considerable change in the spectra of phosphines when they are complexed to metal ions, since the lone pair electrons are then "decoupled" from the phenyl groups by formation of a σ-bond to the metal. The resultant spectra are expected to be similar to those of phosphine oxides, with the $n \rightarrow \pi^*$ transitions blue-shifting. In agreement with expectations, we have observed phenyl vibrational structure in the vicinity of 270 nm for many of the complexes to be discussed later. (A particularly nice example of this effect is the spectrum of $Ir(2\text{-phos})_2H_2^+$, having no low-lying metal-involved transitions, which shows a well-resolved series of sharp phenyl vibronic transitions centered around 265 nm.[78] A useful consequence of this is that the intense ligand $n \rightarrow \pi^*$ transition does not interfere in the spectra of metal complexes.

Delocalization of the phosphorus non-bonding electrons via bond formation imparts a $\delta(+)$ charge to the phosphorus atom, which should contract the diffuse, unoccupied phosphorus d orbitals and might conceivably permit their involvement in π-bonding. Such an effect is, in fact, seen in the phosphine oxides, whose structures are considerably different from those of analogous nitrogen N-oxides, and whose electronic structures probably include considerable $P(d\pi) \leftarrow O(p\pi)$ bonding. In metal complexes, a similar possibility exists for $P(d\pi) \leftarrow M(d\pi)$ bonding, that is, phosphines might function as π-acceptors, and a considerable body of evidence now exists to confirm this possibility.

Studies[79] of the carbonyl frequencies of complexes such as $(R_3P)_3Mo(CO)_3$ have shown a strong correlation of $\nu(CO)$ with the electron-withdrawing character of R, strongly electron-withdrawing R=F, for example, producing much higher $\nu(CO)$'s than R=ethyl. This suggests that PF_3 is a strong π-acceptor. There have been challenges to such rationalizations, suggesting alternative formulations purely in terms of σ-bonding, notably by Venanzi.[80] However, recent structure determinations showing the Cr-O bond length in Ph_3P-$Cr(CO)_5$ to be 0.11Å longer than that in $(PhO)_3P$-$Cr(CO)_5$[81] would seem, in conjunction with the carbonyl frequency work, to have definitely established the importance of π-bonding. (We note that this simply indicates the importance of π-bonding in some metal complexes, and it could be much less important, or not important at all, in complexes of other metal ions.)

A striking example of the effect on phosphine ligand properties of variation of R groups is seen in complexes of Co(III). As we shall see, aryl phosphines seem to produce a Δ comparable to that produced by NH_3. In contrast, trialkyl phosphites seem to produce a Δ comparable to that of cyanide. Thus, the complex CoL_6^{3+}, where L is the tricyclic "melon" phosphite $P(OCH_2)_3CH_3$, has its lowest ligand field band at 325 nm.[82] Such effects cannot be explained in terms of variations in σ-donor capability, as increasing the electronegativity of the R groups would naively be expected to decrease the σ-donor capability. We thus are forced to explain this drastic increase in ligand field strength entirely in terms of π-acceptor capability. (We note that this information does not reveal the importance of π-acceptor capability for the aryl phosphines, although a comparison of the carbonyl frequencies of $(dien)Mo(CO)_3$ and $(Et_3P)_3Mo(CO)_3$[79] indicates that π-bonding may still be quite important, at least for Mo(O).)

The above-mentioned phosphite complex also shows a rather low value of B, which would seem to be a general effect in phosphine complexes. This can be explained purely in terms of σ-effects, the large polarizability of the phosphorus atom allowing for considerable mixing of ligand and metal ion orbitals. (The presumably higher energy of the ligand levels relative to, say, nitrogen, may also be a factor here.) Such mixing, or "covalency" also accounts for the extremely high intensities which have been

observed for ligand field transitions in some phosphine and arsine complexes, ϵ's on the order of 10^3 to 10^4 having been reported.[68]

Phosphine Complexes of d^8 Metal Ions

Prior to discussion of the electronic spectra of phosphine complexes of d^6 metal ions, which are the primary focus of this chapter, we will briefly discuss the spectra of several low-spin d^8 metal ion complexes, which provide several insights into the properties of phosphine ligands. All of the complexes we will consider here are either square planar (or distorted square planar) or square pyramidal 5-coordinate, and thus have coordination sphere geometries similar to those of the distorted octahedral d^6 complexes to be considered later. Occupation of the d_{z^2} metal orbital in these d^8 complexes leads to a simplification of the electronic spectra, both in terms of the number of possible transitions, and in terms of their interpretation.

The complexes $NiLX_2$ and NiL_2X^+, respectively distorted square planar and square pyramidal, have been reported for L=2-phos[70] and 2=phos,[71] with a variety of different X^-, and the electronic spectra discussed. (In several cases, we have reinvestigated the spectra of these complexes, as the original investigators were primarily interested in the ligand field bands and reported charge-transfer bands cursorially or not at all.)

The ligand field spectra of the $NiLX_2$ complexes show a well-resolved transition at ~ 22 kK (possibly corresponding to the

$d_{xz,yz} \rightarrow d_{x^2-y^2}$ transition, but this assignment is unimportant for our purposes), flanked at 4-5 kK to both lower and higher energy by weak shoulders ($\epsilon \sim 10^2$). The energy of the center band varies with X^- in the expected spectrochemical series, and varies for $Ni(2=phos)X_2$,[71] for example, from 22.8 kK for $X^- = CNS^-$ to 21.2 kK for $X^- = Br^-$. In all of these complexes, the extinction coefficient of the transition is about 2000, this large intensity being an example of the intensification effect mentioned at the end of the previous section. Complexes with L=2-phos and L=2=phos have almost identical spectra, the d-d transitions being only 100-200 cm^{-1} higher energy for the 2=phos complexes. (The direction of this shift is consistent with the 2=phos ligand being a slightly stronger π-acceptor, which is certainly rationalizable on the basis of the electron-accepting character of vinyl groups, but the effect is not much, if at all, above noise level.)

Similarly, both 2-phos and 2=phos complexes show a charge-transfer maximum at ~36 kK, the energy also being essentially independent of halide. For $Ni(2\text{-phos})Cl_2$, the band is at 277 nm (36.1 kK) with an ϵ of 22,000. On the low-energy side of this band, at 317 nm (31.5 kK), a shoulder, $\epsilon \simeq 4600$, is evident. We assign the peak at 277 nm to σ charge-transfer from the phosphine to the empty $d_{x^2-y^2}$ metal orbital. In C_{2v} symmetry, there are two such transitions, $^1A_1 \rightarrow {}^1A_1$ and $^1A_1 \rightarrow {}^1B_1$, corresponding to transitions from antisymmetric and symmetric,

respectively, combinations of the two phosphorus lone pairs. We can assign the shoulder at 317 nm to the $^1A_1 \rightarrow {}^1B_1$ transition, which is expected to be weaker than the $^1A_1 \rightarrow {}^1A_1$ transition by reason of much smaller overlap with the $d_{x^2-y^2}$ orbital. As expected, the $^1A_1 \rightarrow {}^1A_1$ is at higher energy, since this is the transition from the bonding phosphorus σ orbital, and the splitting of 4.6 kK is a direct consequence of σ-bonding.

The square pyramidal complexes NiL_2X^+ show ligand field transitions at energies similar to those observed in the $NiLX_2$ complexes, with small shifts of the major transition to lower energy. However, the intense charge-transfer maximum is quite shifted, to ~29 kK. This shift is not as surprising as it might seem at first sight. In D_{4h} symmetry, the phosphine sigma orbitals are a_{1g}, b_{1g}, and e_u, the only parity-allowed electronic transition being $(e_u)^4 \rightarrow (e_u)^3(d_{x^2-y^2})$ ($^1A_{1g} \rightarrow {}^1E_u$). Reduction of symmetry to C_{4V} drops the g,u subscripts and gives a degree of orbital-allowedness to the $(b_1)^2 \rightarrow (b_1)(d_{x^2-y^2})$ ($^1A_1 \rightarrow {}^1A_1$) transition, but, predictably, not very much, as we observe only one transition, with shoulders ascribable to a second transition not being detectable. The point of this is that the only strongly allowed CT transition (and the transition we assign the band at 29 kK to) is a transition from a non-bonding sigma orbital, the e orbital. Thus, the comparison to the previous complexes should be with the weak $^1A_1 \rightarrow {}^1B_1$ transition at ~31 kK, in much better energy agreement. The remaining small discrepancy can be ascribed both to small

differences in the energy of the $d_{x^2-y^2}$ orbital in the two series of complexes, and to ligand-ligand interactions, which could be expected to be noticeably large in a square planar array of atoms as polarizable as phosphorus.

Only a single transition is observed for X^- = Cl^- (28.9 kK, ϵ = 12,200) and Br^- (28.9 kK, ϵ = 13,230) with, however, $Ni(2\text{=phos})_2I^+$ showing two slightly split maxima at 29.57 kK (ϵ = 25,930) and 32.05 kK (ϵ = 26,310).[71] Although confusion with iodide-to-nickel transitions is possible in the last example, a simple explanation of the two maxima is that the ligand e level has been split, as would be expected in the true (C_{2v}) symmetry of the complexes.

Somewhat surprisingly, the complex $Ni(2\text{-phos})_2^{2+}$ also shows two maxima, at 29.7 kK ($\epsilon \simeq 26,000$) and 32.6 kK ($\epsilon \simeq$ 30,000), as shown in figure III-2. The possibility of solution isomerism seems to be ruled out by the observation of two maxima at similar energies in solid state spectra. This suggests that a coplanar NiP_4 arrangement forces greater distortion from 90° P-M-P angles than in the square pyramidal structures, where the Ni(II) ion is, presumably, sitting above the P_4 plane. This is, however, highly speculative. In any case, the spectrum of this complex fully establishes the bands we have observed as arising from phosphorus-to-metal charge-transfer transitions.

The spectra of the 2= phos and 2-phos complexes of Rh(I) and Ir(I) have recently been investigated at low temperature in

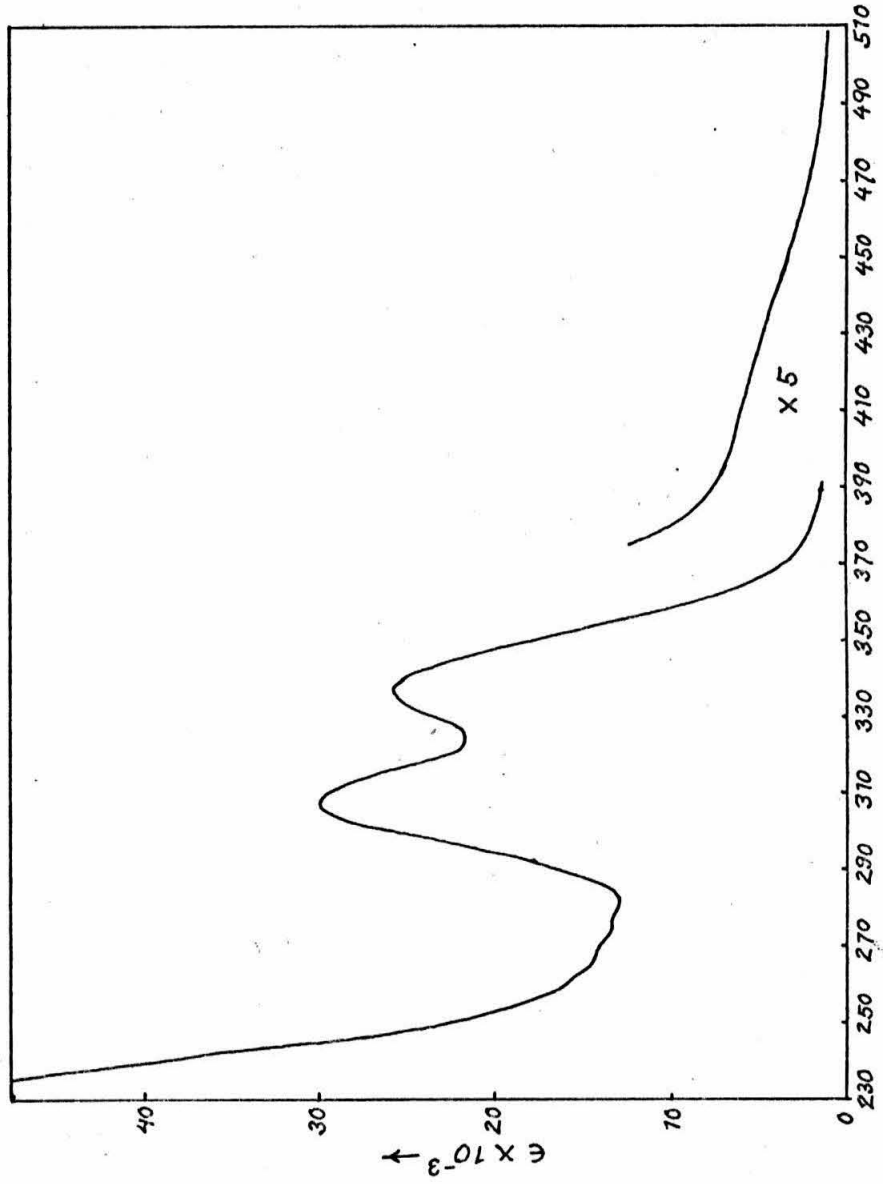


Figure III-2. Electronic spectrum of $[Ni(2\text{-phos})_2](ClO_4)_2$ in CH_2Cl_2, R.T.

these laboratories.[78] As expected from the low oxidation state of the central metal ions, phosphine charge-transfer absorption is shifted far into the UV, and a well-resolved series of ligand field bands is observed in the visible and near ultraviolet. Of interest to our present concern is that the maxima are again nearly identical for the 2-phos and 2=phos complexes (wavelengths agreeing within 5 nm), the only observable difference in the spectra being that a band assignable to the $d_{xz,yz} \rightarrow d_{x^2-y^2}$ transition is resolved into two sharp peaks split by ~1 kK in $Ir(2=phos)_2^+$ and $Rh(2=phos)_2^+$, while the 2-phos analogues show almost no splitting. We conclude that the rigid 2=phos ligand does not allow effective adjustment of the "bite" of phosphine chelation, and therefore forces a larger distortion from D_{4h} symmetry than 2-phos, which can adopt various configurations of the $-(CH_2)_2-$ bridge. We also conclude that this steric constraint is the only spectroscopically observable difference between the two ligands.

Finally, we will consider the ligand field strength of phosphines. A spectrochemical series $R_3P \gtrsim$ piperidine $\gtrsim R_3As$ (the nitrogen donor piperidine producing Δ's slightly lower than those produced by NH_3) has been reported for trans-PtL(piperidine)X_2 complexes.[83] However, this series can only be taken as a very rough guide, for several reasons.

For one, the ligand field strength of phosphines is subject to considerable variation as a function of the electron-withdrawing capacity of substituent groups. Fortunately, hydrocarbon

substituent groups, e.g., alkyl, aryl, and vinyl groups, seem to produce roughly equivalent properties. The ligands 2-phos and 2=phos form metal complexes which are spectrally nearly indistinguishable, while the saturated ligand 1,2-bis(diethylphosphino)ethane forms complexes[84] $NiLX_2$ and NiL_2X having both ligand field and charge-transfer bands shifted only 2 to 4 kK to higher energy, presumably a result of increased σ-bonding due to the slightly more basic alkyl substituents. (It is worth noting that, while strengthening σ-bonding may have the effect of increasing the energy of $L(\sigma) \rightarrow d\sigma^*$ transitions, either by increasing the energy of the $d\sigma^*$ orbital, or decreasing the energy of a ligand σ-bonding orbital, or both, $L(\sigma) \rightarrow d\sigma^*$ transitions could also be blue-shifted in complexes of strongly π-bonding phosphines, simply because the energy of the σ-donor orbital in the free ligand was lower. Comparisons between greatly different phosphines are therefore fraught with peril.)

The ligand field strength of phosphines should also be very much a function of metal ion, particularly if π-acceptor ability is of importance, with increases in the apparent spectrochemical position of phosphines expected for metals in lower oxidation states. This effect necessarily makes comparisons of complexes of different metal ions rather complicated.

Phosphine Complexes of d^6 Metal Ions

We have prepared the complexes trans-$Co(2=phos)_2X_2^+$, X = Cl, Br, and I, by halogen oxidation of the square pyramidal Co(II) complexes $Co(2=phos)_2X^+$ [73] for corresponding X and X_2, and also find that various other derivatives may be obtained by anation reactions with other anions. The survival of the phosphine ligands intact is suggested both by elemental analysis and by infrared spectra of the compounds, which, although complicated, are very characteristic of the ligands. (Metal complexes of 2-phos, for example, can easily be distinguished from those of 2=phos.) The assignment of trans-stereochemistry to the complexes is primarily based on analysis of the low-energy ligand field bands of the complexes (vide infra) and on steric considerations. In the case of the thiocyanate complex, we have an independent criterion in that a single sharp thiocyanate ν(CN) is observed at 2098 cm^{-1}. (We cannot be specific as to the mode of thiocyanate binding in this complex, N- or S-, particularly as a ν(C-S) could not be distinguished in the infrared spectrum. The energy of the observed ν(CN) is probably more consistent with S-bonding, as is the absence of a relatively strong ν(C-S), but these are not very compelling arguments.)

The success of a simple oxidative reaction procedure was actually somewhat unexpected, as Co(III) phosphine complexes are relatively uncommon, and, particularly, we find that the corresponding 2-phos complexes are extremely unstable. Analogous

reactions designed to produce $Co(2\text{-phos})_2X_2^+$, X = Cl and Br, do give very small yields of products having colors appropriate to the desired cations (green for X = Cl and brown for X = Br.) However, they are heavily contaminated with blue and green Co(II) decomposition products (primarily tetrahedral $Co(2\text{-phos})X_2$,[73] X = Cl and Br), and attempted recrystallization leads to complete decomposition. (That traces of the Co(III) products are obtained at all is probably due to their relative insolubility in the reaction medium.)

We do not feel that this drastic difference in stability can be ascribed to electronic differences between the two phosphine ligands, as they seem to form spectroscopically nearly indistinguishable complexes with a variety of metal ions, and an explanation based on steric differences of the ligands seems indicated. It is interesting in this regard that the square pyramidal $Ni(2\text{-phos})_2X^+$ complexes are much less stable than their 2-phos analogues,[70,71] which suggests that, in the Ni(II) complexes, the hydrogens of the dimethylene bridge of 2-phos are a hindrance to axial coordination of an anion.

This steric effect can certainly not be very large energetically, and that it is not a complete explanation is indicated by the fact that we have only been able to prepare $Co(2\text{-phos})_2X_2^+$ complexes where X is a π-donor. All attempts to prepare $Co(2\text{-phos})_2(S)_2^{3+}$, where S is a solvent molecule such as water, acetonitrile, or an alcohol, have failed. We attempted to prepare such complexes by

a variety of methods, including thermal and photochemical solvation of $Co(2=phos)_2X_2^+$ in various solvent mixtures, and oxidation of $Co(2=phos)_2^{2+}$ (for which, see chapter 5) with H_2O_2, $Fe(CN)_6^{3-}$, etc., and always obtained Co(II) decomposition products. Solvation reactions gave steadily increasing deviation from initial isosbestic points, suggesting the decomposition of an initially formed product.

Similarly, $Ni(2\text{-phos})_2^{2+}$ shows no noticeable interaction with coordinating solvents (other than a tendency towards decomposition in strongly coordinating ones), and the stability of the $Ni(2\text{-phos})_2X^+$ complexes is in the reverse order to that expected on steric grounds, the iodide being the most stable, while the chloride is not isolable.[70]

The stable Co(III) phosphine complexes are reminiscent of Co(III) cyanide complexes in showing enhanced stability with "soft" ligands. This behavior can be correlated with the low values of the Racah parameter B observed in both phosphine and cyanide complexes. Cyanocobaltate complexes show a thermodynamic preference for highly polarizable ligands such as iodide, complex formation constants in aqueous solution being large for such ligands.

We have detected phosphine oxides (by infrared and UV spectroscopy) in the decomposition products of the cobalt(III) phosphine complexes, and this suggests that the $Co(2=phos)_2(S)_2^{3+}$ complexes are not simply unstable dissociatively, but <u>oxidatively</u> unstable, most probably by a mechanism involving direct oxidation

of phosphines by the central metal ion. This would be similar to the spontaneous decomposition of $Co(OH_2)_6^{3+}$, which releases hydrogen gas in aqueous solution.

We would thus infer that $CoP_4X_2^+$ complexes are on the borderline of oxidative stability, and that polarizable electron-donor ligands are necessary to prevent spontaneous decomposition.

An oxidative reaction is also suggested for the decomposition of $Co(2\text{-phos})_2X_2^+$ complexes, both by the presence of phosphine oxides in reaction product mixtures, and by formation of $Co(2\text{-phos})X_2$ as a primary decomposition product, whereas $Co(2\text{-phos})_2X^+$ is strongly thermodynamically favored in the presence of two equivalents of the diphosphine.[73] Considering the instability of the $Co(2\text{=phos})_2(S)_2^{3+}$ complexes, the steric factor decreasing $Co(2\text{-phos})_2X_2^+$ stability might be a rather small effect, a "last straw"! We might surmise that the Co-halide bonds are necessarily slightly longer in the 2-phos complexes, and this might lead directly to oxidative instability, or more subtly, might simply increase the reaction rate for dissociation of halide, the solvent complex then remaining the oxidatively unstable species leading to Co(II) products.

The electronic properties we infer for the phosphine complexes are thus drastically different from those of ammine complexes, which is surprising in view of the close similarity in energy observed for d-d bands in cobaltammine complexes and cobalt phosphine complexes. In figure III-3 we show the electronic

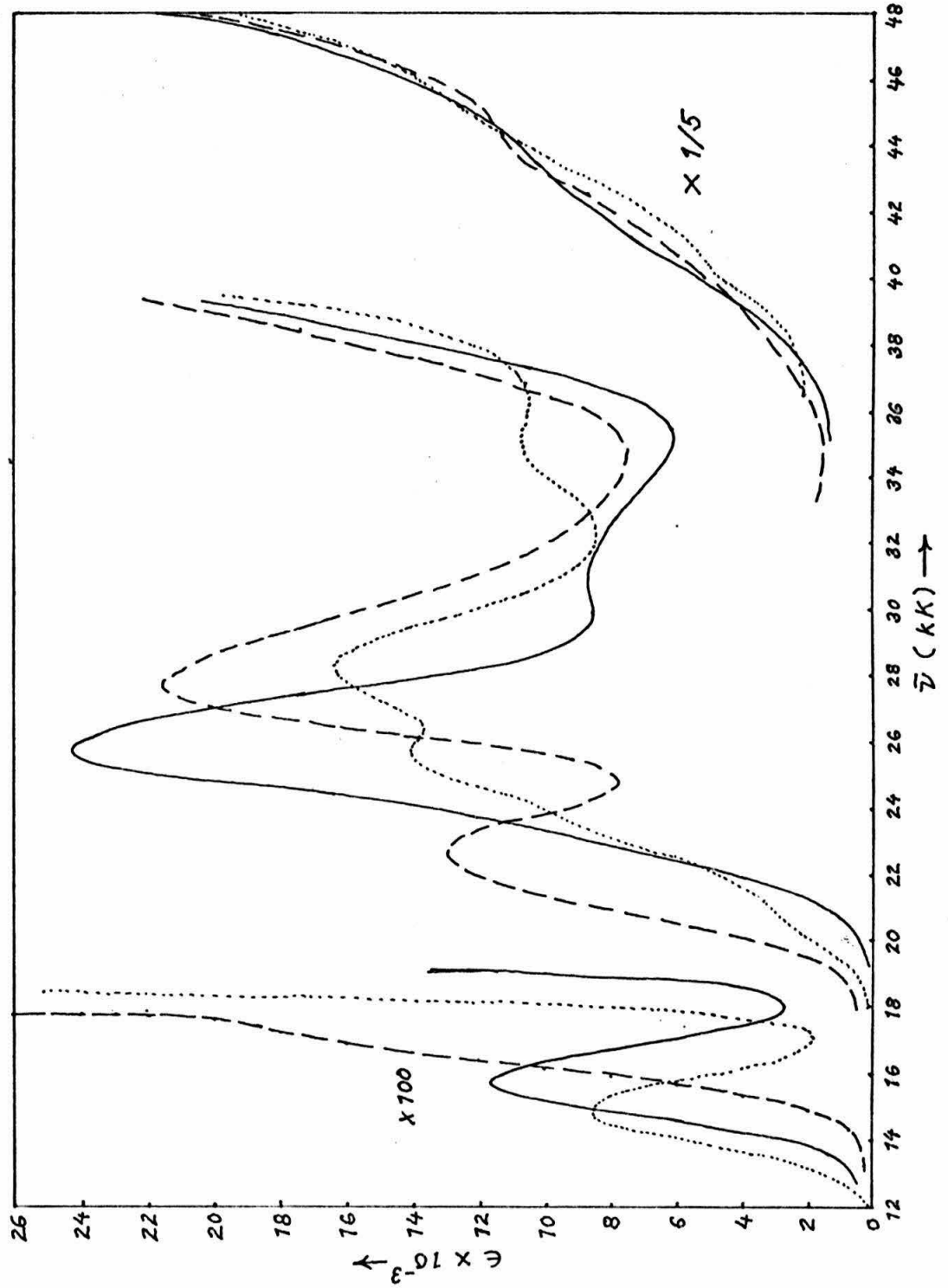


Figure III-3. Electronic spectra of <u>trans</u>-$[Co(2=phos)_2X_2]ClO_4$ in acetonitrile for X^- = Cl^- (——), Br^- (····) and CNS^- (----).

spectra of the complexes trans-$Co(2=phos)_2X_2^+$, $X^- = Cl^-$, Br^-, and CNS^-. Initially, we will focus on the low-energy bands at about 16kK in these complexes.

trans-$Co(en)_2Cl_2^+$ has its $^1A_{1g} \rightarrow {}^1E_g{}^a$ transition at 16.1 kK ($\epsilon = 40$),[85] in remarkably close agreement with the band in trans-$Co(2=phos)_2Cl_2^+$ at 15.9 kK ($\epsilon = 117$), and a similar assignment seems reasonable. The intensity of the transition in the phosphine complex, while being higher than that in the ethylenediamine complex, is still unexceptional for a d-d transition. The assignment to a $d_{xz,yz} \rightarrow d_{z^2}$ transition explains this, as none of the d orbitals involved in the transition interact strongly with the phosphorus sigma-bonding orbitals. (Other explanations which might be invoked for the band not being anomalously intense include the presence of an inversion center in the complex, and the relatively large energy separation of the transition from charge-transfer absorption. However, the large intensities observed for d-d transitions in d^8 complexes, all of which transitions involve $d_{x^2-y^2}$, suggest that these explanations are valueless.)

The $^1A_{1g} \rightarrow {}^1E_g{}^a$ transitions for the other complexes show the expected spectrochemical ordering, $CNS^- > Cl^- > Br^-$. In table III-1 we show the comparison between the energies of the $^1A_{1g} \rightarrow {}^1E_g{}^a$ transitions for en and 2=phos complexes, and also for the trans-$CoAs_4X_2$ chromophores trans-$Co(diars)_2X_2^+$, where diars is the ligand o-phenylenebisdimethylarsine, which show a ligand field of comparable magnitude.

Table III-1

Lowest Energy Absorption Maxima (kK) of

trans-$CoB_2X_2^+$

B/X⁻	Br⁻	Cl⁻	CNS⁻
2=phos	14.9	15.9	17.5
en	15.2[85]	16.1[85]	19.7[85]
diars	15.7[38]	16.4[38]	18.8[38]

Although evaluation of Δ for the complexes strictly requires observation of the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, the relative energy of the $^1A_{1g} \rightarrow {}^1E_g{}^a$ transition still allows us to rank the ligand fields relative to each other, employing relatively few assumptions. (The model outlined in chapter 2 actually predicts the difference in energy of the $^1A_{1g} \rightarrow {}^1E_g{}^a$ transitions for $CoA_4X_2^+$ and $CoB_4X_2^+$ to be $\frac{1}{2}(\Delta(CoA_6^{3+}) - \Delta(CoB_6^{3+}))$. Especially in view of the rather small energy differences observed, however, we cannot place very much faith in this formalism.) We thus find a spectrochemical series $P \lesssim N \lesssim As$. It is amusing that this series is the reverse of that found in reference 83 for platinum(II) complexes. We should reiterate that the ligand field strength of these ligands is dependent on substituent groups (which are dissimilar for the various ligands) and central metal ion, and simply conclude $N \simeq P \simeq As$.

Somewhat larger differences are noted for the thiocyanate complexes, and a spectrochemical series $P < As < N$ is obtained. We suggest (as did Yamada for the diars complex[38]) that this indicates that the phosphine complex probably has S-bound thiocyanates, leading to a sharp decrease in ligand field strength. (This would be similar to the change in bonding between $Co(NH_3)_5NCS^{2+}$ and $Co(CN)_5SCN^{3-}$.)

A study of the ligand field spectra of a variety of Fe(II), Co(III), and Cr(III) diars complexes has been reported.[86] The Fe(II) complexes are quite interesting in that they show a lack

Table III-2

Electronic Spectra of trans-$Co(2\text{=}phos)_2X_2^+$ Complexes

(Solutions in acetonitrile)

Assignment	λ_{max}(nm)	$\bar{\nu}$ (kK)	ϵ
	trans-$Co(2\text{=}phos)_2Cl_2^+$		
$^1A_{1g} \rightarrow {}^1E_g{}^a$ (d-d)	630	15.9	117
$\sigma(P) \rightarrow d_{z^2}$ (?)	440 sh	22.7	7,300
$\sigma(P) \rightarrow d_{z^2}$	338	25.8	24,200
$\sigma(P) \rightarrow d_{x^2-y^2}$	323	31.0	8,700
	trans-$Co(2\text{=}phos)_2Br_2^+$		
$^1A_{1g} \rightarrow {}^1E_g{}^a$ (d-d)	671	14.9	85
$\pi(Br^-) \rightarrow d_{z^2}$	488 sh	20.5	2,600
$\sigma(P) \rightarrow d_{z^2}$ (?)	~435 sh	~23.0	~ 7,000
$\sigma(P) \rightarrow d_{z^2}$	389	25.7	14,000
$\sigma(Br^-) \rightarrow d_{z^2}$	354	28.3	16,300
$\sigma(P) \rightarrow d_{x^2-y^2}$ (?)	285	35.1	10,700
	trans-$Co(2\text{=}phos)_2(CNS)_2^+$		
$^1A_{1g} \rightarrow {}^1E_g{}^a$ (d-d)	570 sh	17.5	192
$\pi(SCN^-) \rightarrow d_{z^2}$	442	22.6	12,900
$\sigma(P) \rightarrow d_{z^2}$	360	27.8	21,500
$\sigma(P) \rightarrow d_{x^2-y^2}$	~325 sh	~31.0	~12,000

of charge-transfer absorption and, correspondingly, show a full set of d-d transitions. (We have prepared and briefly investigated $Fe(2=phos)_2Cl_2$, which similarly shows no charge-transfer absorption below the onset of ligand absorption.) The spectrum of $Fe(diars)_3^{2+}$ shows a $^1A_{1g} \rightarrow {}^1T_{1g}$ transition at 21.4 kK, whereas $Co(diars)_3^{3+}$[38,86] has its $^1A_{1g} \rightarrow {}^1T_{1g}$ transition at 23.2 kK, indicating Δ(Fe(II)) to be only slightly smaller than Δ(Co(III)). A similar effect has been noted[57] in $Fe(CN)_6^{4-}$ versus $Co(CN)_6^{3-}$, and can be ascribed to an enhanced importance of π-donation in the Fe(II) complexes due to the lower oxidation state. (The ligand field parameter B of 325 cm^{-1} evaluated for $Fe(diars)_3^{2+}$ is extraordinarily low, the value of 400 cm^{-1} for $Fe(CN)_6^{4-}$ [57] being already very low.)

The $Co(2=phos)_2X_2^+$ complexes, in contrast, have rich charge-transfer spectra, which can confidently be assigned as ligand-to-metal by reference to the Fe(II) complexes. We consider $Co(2=phos)_2Cl_2^+$ first. The corresponding ethylenediamine complex has its lowest (chloride(π)) charge-transfer band at 32.5 kK (ϵ = 1300),[85] so the bands observed should be phosphine-to-metal. (See later, however.)

In D_{4h} symmetry we expect two orbitally-allowed phosphine (σ)-to-metal transitions, $e_u^2 \rightarrow e_u d_{x^2-y^2}$ and $e_u^2 \rightarrow e_u d_{z^2}$, both being $^1A_{1g} \rightarrow {}^1E_u$. The transitions are thus directly analogous to the case of pseudohalide π charge-transfer considered in chapter 2. The spectrum shows two intense bands at 25.8 kK (ϵ = 24,200) and

31.0 kK (ϵ = 8,700) which we assign, respectively, to the transitions to d_{z^2} and $d_{x^2-y^2}$. The observed splitting of 5.2 kK is reasonable for the d_{z^2} - $d_{x^2-y^2}$ splitting in tetragonal symmetry. The second band is relatively close to the energy of <u>trans</u>-$Co(en)_2Cl_2^+$ chloride(π) charge-transfer, but the intensity is rather high for such an assignment, and there is no obvious rationale for "anomalous" intensity of a $Cl(\pi) \rightarrow d_{z^2}$ transition, which should be relatively free of admixture with phosphine σ orbitals.

A shoulder is observed on the low energy side of the charge-transfer bands, at ~ 23 kK ($\epsilon \simeq 8000$). Several assignments are possible, including as an orbitally forbidden $P(\sigma) \rightarrow$ Co transition, or as a split component of the $e_u^2 \rightarrow e_u d_{z^2}$ transition. A particularly interesting possibility is that this is the $^1A_{1g} \rightarrow {}^1A_{2g}$ ligand field transition, which might show an anomalously large intensity (being $d_{xy} \rightarrow d_{x^2-y^2}$, formally), and which appears at 22.5 kK for <u>trans</u>-$Co(en)_2Cl_2^+$.[19] The various possibilities are difficult to distinguish, however, and no definite assignment can be given. A (less well-resolved) shoulder is observed at similar relative energy in the corresponding Rh(III) complex (<u>vide infra</u>) and this seems slightly more supportive of an orbitally forbidden CT assignment. Assignment as a split component of the allowed charge-transfer transition is least likely, as there is no obvious reason why two split components should show such markedly unequal intensities.

We attempt no assignment of the high energy portion of the spectrum (36 kK to 48 kK) for this or any of the following complexes,

both because of the poor resolution observed and because of the presence of strong intra-ligand absorption in this energy range.

The complex trans-$Co(2\text{=}phos)_2(CNS)_2^+$ has an intense band at 27.8 kK (ϵ = 21,500) which we can assign to the $e_u^2 \rightarrow e_u d_{z^2}$ transition, with the extremely unsymmetrical high energy tail of the band giving clear evidence of a $e_u^2 \rightarrow e_u d_{z^2}$ transition at 30-31 kK. We expect the $e_u^2 \rightarrow e_u d_{z^2}$ transition to shift to higher energy in the thiocyanate complex, as the magnitude of the tetragonal distortion has decreased, and the shift of the transition to higher energy from that of the trans-dichloride of 2.0 kK is reasonable. (We can expect a much smaller shift of the transition to $d_{x^2-y^2}$, as observed.) This, however, leaves us with the considerable problem of the assignment of the transition observed at 22.7 kK (ϵ = 12,900). Assignment as a very split component of phosphine charge-transfer or as a tremendously anomalously intense ligand field transition does not have much to recommend it.

We feel that the only reasonable assignment of this peak is as thiocyanate-to-metal charge-transfer, in spite of the low energy of the band. (The complex trans-$Co(en)_2(NCS)_2^+$ has the transition $\pi(NCS^-) \rightarrow$ Co at 30.9 kK.[87] Although this is an N-bound complex, while the phosphine complex is probably S-bound, the $\pi \rightarrow d\sigma^*$ transition should not be at very different energy for the different linkage isomers, c.f. results presented in chapter 2.) The intensity of the band is reasonable for this assignment if the thiocyanate is

S-bound. The 22.7 kK band would correspond to $\pi(SCN^-) \rightarrow d_{z^2}$, with the $\pi(SCN^-) \rightarrow d_{x^2-y^2}$ transition (which was relatively weak in the cyanide complexes of chapter 2) predicted to lie at about the same energy as the intense $\sigma(P) \rightarrow d_{z^2}$ transition, and therefore being unobserved.

Alternatively, we might assign the two intense charge-transfer maxima as split components of the $\sigma(P) \rightarrow d_{z^2}$ transition. However, the necessary splitting of 5.1 kK seems extraordinarily large in view of the apparently small splitting in the trans-dichloride, especially for an N-bound isomer. For an S-bound isomer, such a large splitting could perhaps be countenanced (although it would still be quite surprising) but the assignment would have the unfortunate consequence of leaving no intense bands assignable as $\pi(SCN^-) \rightarrow d_{z^2}$.

The extremely complicated charge-transfer spectrum of trans-$Co(2\text{=}phos)_2Br_2^+$ could be tentatively assigned as follows. The peak at 35.1 kK (ϵ = 10,700) is at about the same energy as the $\sigma(Br^-) \rightarrow d_{z^2}$ transition observed for trans-$Co(en)_2Br_2^{+}$[85] (34.6 kK, ϵ = 22,000) and might be assigned similarly. The two intense lower energy charge-transfer peaks at 28.3 kK (ϵ = 16,300) and 25.7 kK (ϵ = 14,000) could then be assigned as split components of the $\sigma(P) \rightarrow d_{z^2}$ transition, the splitting presumably arising from the larger ionic radius of bromide, and the two shoulders at lower energy could be assigned as forbidden phosphorus charge-transfer or ligand field transitions.

However, an interesting alternate set of assignments exists. If halide and pseudohalide charge-transfer could be assumed to lie at ~8000 cm^{-1} lower energy in the phosphine complexes than in the ethylenediamine complexes, as suggested by the spectrum of the thiocyanate complex, then we could assign the shoulder at 20.5 kK (ϵ = 2,600) to $\pi(Br^-) \rightarrow d_{z^2}$ charge-transfer. This transition is seen at 28.1 kK (ϵ = 2,200) in trans-$Co(en)_2Br_2^+$.[85] One of the two intense transitions between 25 and 28 kK could then be assigned to the $\sigma(Br^-) \rightarrow d_{z^2}$ transition, most likely that at 28.3 kK, as we expect the $\sigma(P) \rightarrow d_{z^2}$ transition to be slightly red-shifted from that of the trans-dichloride, and could therefore assign the peak at 25.7 kK to this transition. The shoulder at ~23 kK ($\epsilon \simeq$ 7,000) could be assigned in the same way as was the shoulder at about the same energy in the trans-dichloride.

In this scheme, however, the peak at 35.1 kK is not assigned with ease. Assignment to $\sigma(P) \rightarrow d_{x^2-y^2}$ seems unsatisfactory because of the poor agreement with this transition in the trans-dichloride. If the 35.1 kK peak is not this transition, we remain free to postulate a relatively weak and unresolved $\sigma(P) \rightarrow d_{x^2-y^2}$ transition at ~31 kK. However, no other obvious assignment presents itself.

Either set of assignments must be considered to be rather artificial, and not to be taken very seriously. Our only reliable conclusion is an estimation of the energy of $\sigma(P) \rightarrow d\sigma^*$ charge-transfer transitions, primarily based on the spectrum of the

trans-dichloride, with the low-energy band of the thiocyanate complex remaining temptingly suggestive of very low-energy thiocyanate charge-transfer absorption. If we could confidently so assign these spectra, the shift of $\sim 8000\ cm^{-1}$ would lead to the extraordinary conclusion that nearly one-third of the ligand field splitting in the phosphine complexes is due to π-acceptor interactions of the phosphines, given a value of ~ 25 kK for Δ in cobaltammine complexes[31] (for which Δ can reasonably be assumed to arise purely from sigma-donor interactions.) Such π-acceptor bonding would give considerably lower energy empty "e_g" metal orbitals (that is, a considerably more oxidizing central Co(III) ion) than in the ammine complexes, while allowing for a similar ligand field splitting. Unfortunately, we cannot be so confident. In any case, we simply wish to emphasize the rather obvious point that ligand field parameters give us no information as to the relative importance of π- and σ-bonding in low-spin d^6 complexes, and the spectrochemical similarity of nitrogen, phosphorus, and arsenic ligands is unexceptional in this regard in not excluding π-bonding. A π-acceptor component of the electronic structure of metal ions, especially in high oxidation states, has not been much in favor in recent years,[82,86] but we do not feel that any firm evidence in this regard has yet been presented.

The charge-transfer spectra of diars complexes of Co(III) can be assigned as were those of the phosphine complexes. The

electronic spectrum of $Co(diars)_3^{3+}$[38,86] shows a single intense charge-transfer band at 32.0 kK, which may be assigned as $t_{1u} \rightarrow t_{2g}$ ($\sigma(P) \rightarrow d\sigma^*$). The complex trans-$Co(diars)_2Cl_2^{+}$[38] has two bands at 25.5 kK and 31.0 kK, which can be assigned as the transitions from the arsenic $e_u(\sigma)$ level to d_{z^2} and $d_{x^2-y^2}$, respectively. The good agreement of the energy of the later transition with that of the $Co(diars)_3^{3+}$ transition is rather pleasing. The complex trans-$Co(diars)_2(CNS)_2^{+}$[88] has two bands at energies similar to those of the trans-dichloride transitions, which can again be assigned to $\sigma(As)$ charge-transfer transitions, and also a band at 19.6 kK, which we might again assign to thiocyanate charge-transfer.

The "optical electronegativity" of the arsenic ligand is therefore quite comparable to that of the phosphorus ligand (perhaps slightly lower), and very much less than that of nitrogen ligands. The depressed energy of the thiocyanate LMCT transition could indicate that the arsenic ligand is a π-acceptor in its Co(III) complexes, even more so than the phosphorus ligand is. (We note, incidentally, that steric hindrance should be much less in the diars complexes, and assignment of the band in the thiocyanate complex to a split component of $\sigma(As)$ LMCT therefore seems extremely unlikely.) If our second set of assignments of the charge-transfer spectra is correct in detail, then the energy of the $\sigma(As)$ and $\sigma(P)$ charge-transfer would be comparable to (and slightly less than) that of $\sigma(Br^-)$ charge-transfer, whereas if the ligand-field splitting is completely due to sigma-donor interactions, the charge-transfer would necessarily correspond to a much lower optical

electronegativity, comparable to $\pi(Br^-)$ charge-transfer. It seems likely that study of phosphine derivatives of well-studied ML_5X series (the $Co(CN)_5X^{n-}$ series, for example) would settle this question. (The spectra of $P(C_6H_5)_3$ and $As(C_6H_5)_3$ derivatives of $Fe(III)(CN)_5X^{n-}$ have been reported,[89] and show low-energy charge-transfer bands, but the cyanoferrate complexes are not very suitable for detailed comparisons such as this one, their spectra showing very large solvent shifts,[90] and many of the complexes, particularly the halide derivatives, showing very poor stability.)

In figure III-4 we show the electronic spectrum of trans-$Rh(2=phos)_2Cl_2^+$ at room temperature and 77°K. The band at 24.2 kK (ϵ = 460) (which shows a decrease in intensity and shift to higher energy at 77°K, both effects being in part due to sharpening of the charge-transfer band it is shouldered on) is assigned as $^1A_{1g} \rightarrow {}^1E_g{}^a$. In comparison, trans-$Rh(en)_2Cl_2^+$ shows this transition at 24.6 kK (ϵ = 75),[91] while trans-$Rh(diars)_2Cl_2^+$ shows a band at 24.7 kK (ϵ = 186).[38] A well-resolved charge-transfer band is seen at 31.2 kK (ϵ = 32,350) at room temperature, and may be assigned to $\sigma(P) \rightarrow d_{z^2}$, the shift to higher energy relative to the cobalt complex of 5.4 kK comparing favorably to the shifts we observed in chapter 2 for $M(CN)_5X^{3-}$ LMCT transitions. The expected $\sigma(P) \rightarrow d_{x^2-y^2}$ transition is presumably buried under ligand absorption, which is indeed rather more intense than expected. At low temperature, shoulders are poorly resolved to both high and low

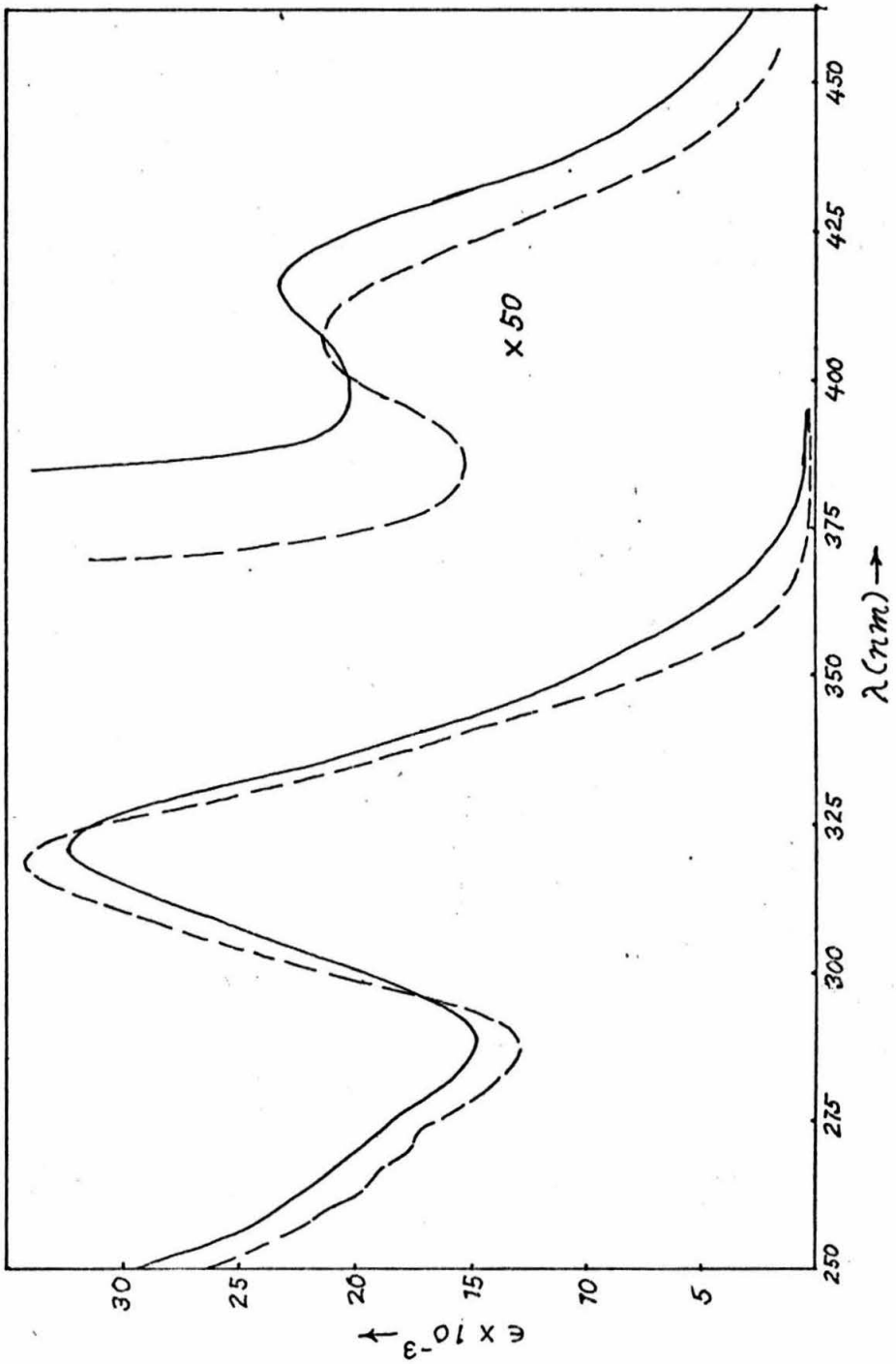


Figure III-4. Electronic spectra of trans-$[Rh(2=phos)_2Cl_2]ClO_4$ in 6:1 EPA-CH_2Cl_2 at R.T. (——) and 78°K (----).

energy of the charge-transfer peak. That at ~ 33 kK might correspond to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, as $Rh(NH_3)_6^{3+}$ has its $^1A_{1g} \rightarrow {}^1T_{1g}$ transition at 32.7 kK.[91] The shoulder at ~ 30 kK may have the same explanation as the analogous shoulder in the Co(III) complex, which we discussed earlier.

We have also been able to prepare the analogous 2-phos complex, trans-$Rh(2\text{-phos})_2Cl_2^+$. Re-emphasizing our previous points as to the electronic similarity of the 2-phos and 2=phos ligands, the spectrum of this complex is almost identical to that of the 2=phos complex.

We have observed emission from the Rh(III) complexes, both from the solids (at R.T. and 77°K) and from glassy solutions of the compounds at 77°K. In figure III-5 we show the emission observed from trans-$Rh(2\text{=phos})_2Cl_2^+$ in glassy solution at 77°K, which has a maximum at 17.0 kK. The pure solid has an emission maximum at 16.8 kK at R.T., shifting to 17.1 kK at 77°K. The long wavelength tail of the emission seems to show some structure, but the sensitivity of our instrument is low in the near-infrared, and we reserve comment. The 2-phos complex has similar emission.

In figure III-6 we show the corrected (for the spectral distribution of the exciting source) excitation spectrum of trans-$Co(2\text{=phos})_2Cl_2^+$ at 77°K. The agreement of the excitation spectrum with the absorption spectrum is striking, and strongly indicates that the charge-transfer states decay efficiently to the low-lying ligand field states, e.g., inter-system cross. (In

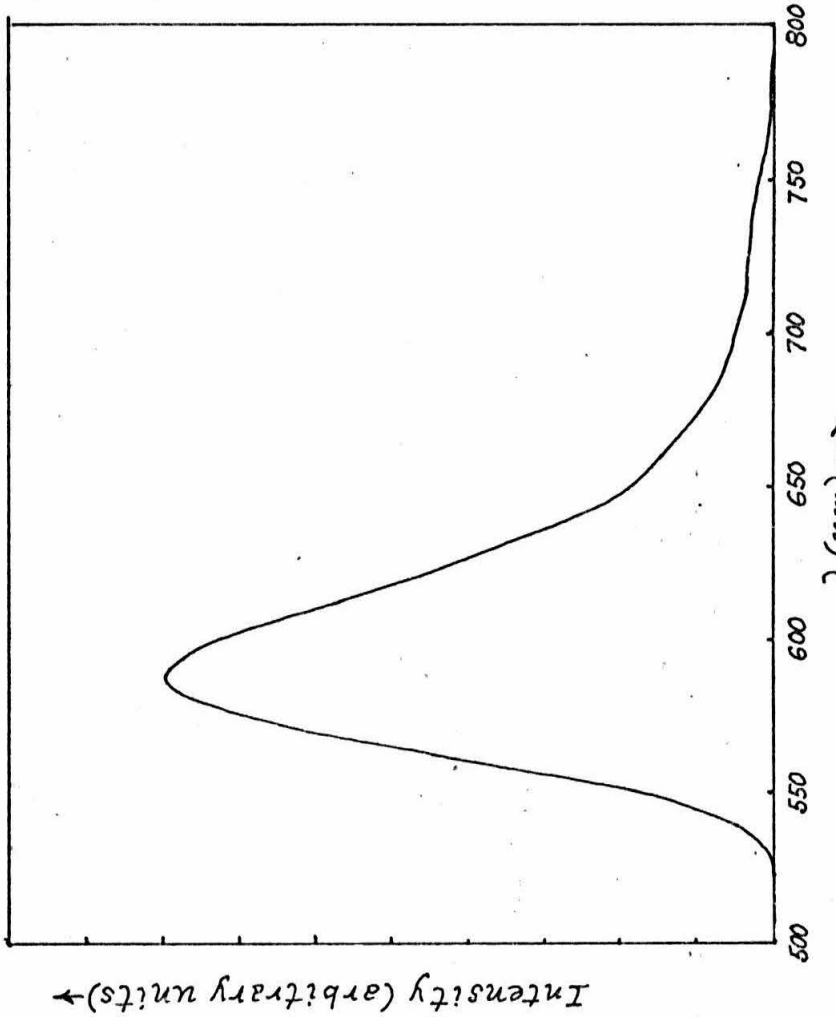


Figure III-5. Emission spectrum of trans-$[Rh(2=phos)_2Cl_2]ClO_4$ at 78°K in 6:1 EPA-CH_2Cl_2.

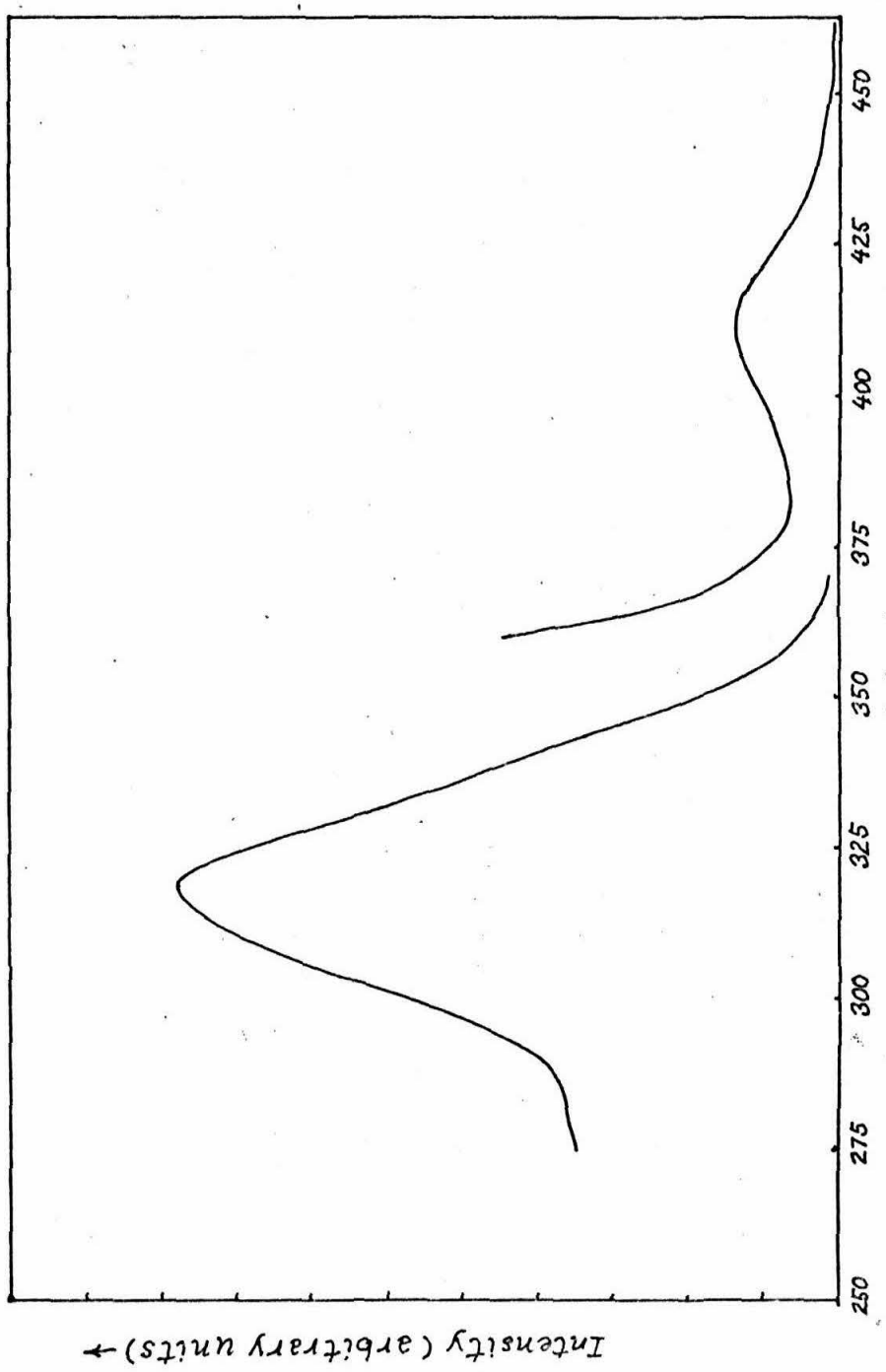


Figure III-6. Corrected excitation spectrum of trans-$[Rh(2=phos)_2Cl_2]ClO_4$ in 6:1 EPA:CH_2Cl_2 at 78°K.

contrast, the ligand-localized states may decay to the ground state by other routes, but we were not able to obtain good enough data at high energies to be sure on this point.)

The emission is presumably $^3E_g{}^a \rightarrow {}^1A_{1g}$. Demas and Crosby[92] observed emission from <u>trans</u>-$Rh(py)_4Br_2^+$ at 14.6 kK, with a measured lifetime characteristic of spin-forbidden emission, and were able to observe a weak band in absorption at ~ 20.3 kK ($\epsilon \simeq 3$), assigned as $^1A_{1g} \rightarrow {}^3E_g{}^a$, which indicates a reasonably small Stokes shift between emission and absorption of 5.7 kK. For our complex, although the triplet band remains unobserved, we expect it to be at ~ 22 kK, assuming a similar triplet-singlet separation, which would give a similarly small Stokes shift.

The observation of "normal" emission in this complex is actually of great interest, as the charge-transfer absorption is very low-energy relative to d-d absorption. One explanation which has been proposed for the preponderance of redox reactions in the photochemistry of cobaltammine complexes is that the charge-transfer states are very "expanded" at equilibrium nuclear distances, and thus have lower energy than ligand field states that have lower vertical excitation energies than the charge-transfer state vertical excitation energies.[59] In this complex, vertical charge-transfer is rather closer in energy to the lowest singlet d-d transition than in most cobaltammine complexes, yet we observe entirely normal metal-localized emission, and an excitation spectrum identical to the absorption spectrum, implying that the

relaxed charge-transfer state is not very "expanded." The generality of our conclusion is, of course, drastically restricted by the fact that the ligand involved in the charge transfer is a chelating ligand, and the charge-transfer is distributed over four phosphorus atoms. However, this still remains an observation (rather uncommon) of excitation into a LMCT band leading to d-d emission.

Finally, we will consider the spectroscopy of cis-$CoP_4X_2^+$ chromophores. We were unable to prepare such compounds with the 2=phos ligand, and a cis-geometry is probably prohibited by the steric constraints of the ligand. (An attempt to prepare a cis-dichloride from the bonafide cis-complex $Co(2=phos)_2O_2^+$ gave the trans-dichloride.) However, the complex cis-$Co(QP)Cl_2^+$, where QP is tris(o-diphenylphosphinophenyl)phosphine, has been reported,[93] and its spectrum may be taken to be representative of cis-$CoP_4X_2^+$ chromophores.

A band which can be assigned as the "$^1A_1 \rightarrow {}^1E^a$" transition is reported at 20.4 kK (ϵ = 5600), to be compared to the analogous transition of cis-$Co(en)_2Cl_2^+$ at 19.3 kK.[38] The large intensity of the cis-$Co(QP)Cl_2^+$ band is understandable, as phosphorus σ-orbital mixing is expected with both metal $d\sigma^*$ orbitals in this symmetry. Also, the complex can be expected to be rather distorted by the "tripod" QP ligand, with even larger intensities resulting. A charge-transfer transition is observed at 31.0 kK (ϵ = 16,600), and can be assigned as $P(\sigma) \rightarrow d\sigma^*$. Exact assign-

ment of this transition is difficult, as all eight possible $P(\sigma) \rightarrow d\sigma^*$ transitions are formally allowed in C_{2v} symmetry. Actually, the symmetry is not effectively broken down this far, which is why we can generally speak of a "$^1A_1 \rightarrow {}^1E^a$ ligand field transition."[30] However, we should still describe the transition only as $P(\sigma) \rightarrow d\sigma^*$ ($d_{x^2-y^2}$ and d_{z^2} are inappropriate as labels for the d orbitals in this symmetry) and note that it occurs at about the same energy as the $P(\sigma) \rightarrow d_{x^2-y^2}$ transition in the trans-complexes (a shift to higher energy, relative to the trans-complex, of the lowest charge-transfer band having been expected.) A poorly resolved shoulder is observed at 37.5 kK ($\epsilon \sim 16,000$) which may be another $P(\sigma) \rightarrow d\sigma^*$ transition, or might simply be ligand absorption.

The cis-isomer of $Co(diars)_2Cl_2^+$ has also been reported,[94] and has its "$^1A_1 \rightarrow {}^1E^a$" peak at 20.4 kK ($\epsilon = 630$), in good agreement with the energy of the transition in cis-$Co(QP)Cl_2^+$.

Thus, as for the trans-complexes, we have a reasonable understanding of the electronic spectra of the cis-complexes, and can expect the lowest ligand field band of a cis-CoP_4X_2 chromophore to be at about the same energy as the corresponding band in cis-CoN_4X_2 chromophores, with enhanced intensity. We can, furthermore, expect the lowest intense $\sigma(P) \rightarrow d\sigma^*$ charge-transfer transition to be at ~ 30 kK. The reliability of these conclusions, based on limited data, is, of course, much increased by the consistency of the spectra of the trans-complexes.

CHAPTER IV

Complexes of "End-On" Bound Dioxygen

Introduction

In 1852, Fremy[95] reported a new complex, isolated from oxygenated ammoniacal cobalt(II) solutions, which he formulated as a μ-peroxodicobalt(III) salt. The succeeding years have seen a tremendous increase in the number of binuclear cobalt complexes reported, most notably as part of the classic work of Werner[96] and his students. These years have also seen, eventually, the complete confirmation of Fremy's original formulation of his compound.

In this chapter, we will consider the electronic structures of a variety of metal complexes of dioxygen ligands which are bound to a metal ion by a single oxygen, for which we employ the term "end-on" bound dioxygen, avoiding any implied reference to the electronic details of the binding. We will concentrate on dioxygen bridged dicobalt complexes, which a variety of structural and spectroscopic investigations (many of which we will refer to in the following discussion) have by now shown rather conclusively to be cobalt(III) complexes with either peroxide or superoxide bridges. We will attempt to extend this study to various monomers and also to complexes of other metal ions.

A preliminary version of many of the results to be presented herein appeared in the Ph.D. thesis of Irving Treitel.[17] Within the context of his research, we studied these complexes

primarily from the viewpoint of a general investigation of the interaction of metal ions in binuclear complexes. We concluded that the metal ions in these complexes were essentially non-interacting, that is, that the d-d transitions observed were distinctly those of an isolated metal ion, and also arrived at some rather novel characterizations of the spectrochemical properties of dioxygen ligands and of the charge-transfer spectra of the complexes. We will now extend and elaborate on the conclusions we arrived at.

Experimental

Preparation of Compounds

$[(NH_3)_5CoO_2Co(NH_3)_5]SO_4(HSO_4)_3 \cdot H_2O$ was prepared by a literature procedure.[97,98]

Analysis:

Calcd: Co, 16.28; S, 17.66; N, 19.31; H, 4.82

Found: Co, 16.43; S, 17.30; N, 19.11; H, 4.90.

$[(NH_3)_5CoO_2Co(NH_3)_5]Cl_4 \cdot 4H_2O$ was prepared by the method of Linkard and Weigel.[99] Two crystalline forms are obtained on recrystallization, very fine needles from concentrated solutions and flat plates from dilute solutions. The larger crystals show a much higher apparent stability, the fine needles turning red within a few days.

The $(NH_3)_5CoO_2Co(NH_3)_5^{4+}$ ion was prepared as the sulfate salt by the method of Schaeffer,[100] and also as the nitrate salt.[101] Preparations as the nitrate salt gave far superior

products in our hands, fresh products being entirely homogeneous on microscopic examination, and consisting of well-formed yellow-brown prisms. On standing in air at room temperature, the compound acquired a greenish color and otherwise showed evidence of decomposition. Measurements were done on fresh preparations which were stored at -5 °C.

$K_5[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$ was prepared by a published method,[102] using $[(NH_3)_5CoO_2Co(NH_3)_5]SO_4(H_2SO_4)_3 \cdot H_2O$ as a starting material. Very careful fractional recrystallization with ethanol and methanol at -5 °C afforded large dendritic magenta crystals, which appeared "scaley" on microscopic examination. No other cation (Na^+, NH_4^+, Ba^{2+}, and $(C_4H_9)_4N^+$ were tried) gave crystalline products. A considerable effort was made to obtain single crystals suitable for an X-ray structural determination, but met with no success.

Analysis:

Calcd: Co, 18.90; C, 19.26; N, 22.46; K, 31.35; H, 0.32.

Found: Co, 17.81; C, 19.53; N, 20.89; K, 28.81; H, 0.77.

$K_6[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$ was prepared by the method of Haim and Wilmarth.[103]

Analysis:

Calcd: Co, 17.79; C, 18.12; N, 21.14; H, 0.30.

Found: Co, 16.46; C, 18.06; N, 21.00; H, 0.57.

$Ba_3[(CN)_5CoO_2Co(CN)_5] \cdot 3H_2O$ was prepared from the above potassium salt by the method of Roberts and Symes,[104] and could

be obtained as large, well-formed orange crystals. However, our commercial elemental analyses were quite poor.

The $[(NH_3)_5Co(O_2H)Co(NH_3)_5]^{5+}$ ion was prepared as its sulfate salt by treatment of either the nitrate or sulfate salt of the μ-peroxo decaammine cation with ice-cold 3M sulfuric acid.[105] This red compound is also rather unstable at room temperature, and was stored at -5 °C.

Bis(salicylaldehyde)ethylenediimine cobalt(II) was prepared by I. M. Trietel.

The peroxide complex of ferric EDTA was prepared in solution by a published procedure.[106]

The oxygenated complex of ruthenium EDTA was prepared by a modification of a published procedure.[107] $K_2RuCl_5(OH_2)$, prepared by the method of Mercer and Buckley,[108] was boiled in solution with an equimolar quantity of K_2EDTA. Reduction of volume gave a lemon-yellow crystalline product which was recrystallized from 6N HCl to give $K[Ru(H_2EDTA)Cl_2]$ as golden microcrystals.

Analysis:

Calcd: Ru, 20.16; K, 7.79; Cl, 14.14; C, 23.95; H, 2.81; N, 5.58.

Found: Ru, 21,53; K, 8.82; Cl, 15.05; C, 24.18; H, 2.97; N, 5.93.

Reaction of a solution of the above compound with an equimolar amount of silver oxide gave a precipitate of silver chloride.

Addition of an equivalent of KOH then gave a red-brown solution of the "hydroxo" complex, which turned deep yellow-green after air was bubbled through it for 24 hours. All attempts to isolate pure solids from such solutions failed, reduction of volume, addition of non-aqueous solvents, or attempted precipitation with various cations and anions giving, at best, visibly decomposed powders or intractable oils. (On one occasion, addition of isobutanol and maintenance at 0 °C overnight gave a few small deep green needle crystals. However, these rapidly oiled when removed from the mother liquor.)

Measurements

Spectra measurements were done as described previously. For measurements of the visible and ultraviolet spectra of compounds in KBr pellets, the compound was very finely ground with KBr (generally, ~300 mg) and the mixture pressed into a pellet, which was reasonably transparent to 220 nm if prepared carefully. Spectra were measured using KBr reference pellets of the same thickness. Pellets could be cooled to ~80 °K in a brass holder, the bottom of which was immersed in liquid N_2.

Thermal decomposition rates of complexes were measured spectrophotometrically in the sample compartment of the Cary 17, employing a cell holder adapted to circulate water from a thermostated water bath continuously around the cell.

Disappearance quantum yields for $(CN)_5CoO_2Co(CN)_5^{5-}$ were determined as described in chapter 2, the concentration of the anion

being monitored by following the decrease in absorbance at 485 nm.

Results and Discussion

Co(III) Peroxide Complexes

Many Co(II) complexes take up molecular oxygen in aqueous solutions, and binuclear μ-peroxo complexes are often isolable. As noted in the introduction, the complex formed from cobalt(II)/ammonia solutions is a rather well-known example, and this complex can be readily isolated as crystalline salts of various anions. It has long been known that the complex is diamagnetic,[109] indicating that the O_2 group is strongly bound. The best evidence for the complex's formulation as a μ-peroxodicobalt dimer, however, comes from the recent X-ray structural determination by Schaeffer[100] of the disulfate tetrahydrate salt. The cation, $(NH_3)_5CoO_2Co(NH_3)_5^{4+}$, shows a non-linear, non-planar, four atom CoO_2Co chain, with a structure reminiscent of hydrogen peroxide. The torsional angle about the O_2 direction is $\sim 146°$, somewhat greater than that in H_2O_2, but presumably the smallest torsional angle possible without primary bond angle distortion resulting from steric interaction of the two $Co(NH_3)_5$ units. The O_2 bond distance of 1.47 Å is quite typical of O_2^{2-} ions, while the Co-N bond distances are characteristic of Co(III) (rather than Co(II).) The structure of the complex thus seems to conclusively indicate a rather more than formal transfer of two electrons from Co(II) ions to a dioxygen molecule in the ground state of the complex.

In ammonia solution, the oxygenation reaction is rapid and completely reversible [110] (although side reactions, principally the further oxidation of the μ-peroxo dimer to the μ-superoxo dimer to be discussed later, limit the reversibility over many cycles.) The kinetics of the reaction implicate a reactive intermediate monomer, $Co(NH_3)_5O_2^{2+}$, which has, however, never been directly detected. In figure IV-1, we show the electronic spectrum of a solution of the ion in 7 M aqueous ammonia saturated with O_2. (This solution was actually prepared from the pure crystalline nitrate salt, but could as easily have been prepared from a Co(II) salt dissolved in 7 M aqueous ammonia.) Under these conditions, ~10% of the cobalt in the solution is present as the μ-peroxo dimer. Bubbling N_2 through the solution regenerates Co(II), which at this concentration shows a weak featureless rising absorption curve. The spectrum shown is thus characteristic of the dimer.

Two relatively intense peaks are observed at 359 nm ($\epsilon \simeq 3000$), and 290 nm ($\epsilon \simeq 3700$). (The ϵ's quoted were obtained by reference to the equilibrium data of Simplicio and Wilkins, [110] and are crudely corrected for Co(II) absorption.) These bonds are logically assigned as charge-transfer transitions from the filled π^* level of bridging peroxide to the empty Co(III) $d\sigma^*$ levels. The two transitions observed could conceivably be assigned as transitions to d_{z^2} and $d_{x^2-y^2}$, but the large splitting of 6.6 kK observed is not at all consistent with the high energy of the lowest d-d band (vide infra), which indicates a small $d\sigma^*$ splitting. On the other hand,

Figure IV-1. Electronic spectrum of $(NH_3)_5CoO_2Co(NH_3)_5^{4+}$ in concentrated aqueous NH_3.

Table IV-1

Electronic Spectra of Co(III) Peroxide Complexes

	Assignment	λ_{max}(nm)	ν_{max} (kK)	ϵ/formula unit
$(NH_3)_5CoO_2Co(NH_3)_5^{4+}$	l.f. $^1A_1 \rightarrow \{^1E^a, {}^1A_1\}$	~500 (w.sh.)	~20	~500
7M aq. NH_3, R.T.	$\pi^*(O_2^{2-}) \rightarrow d\sigma^*$	359	27.9	~3000
	$\pi^*(O_2^{2-}) \rightarrow d\sigma^*$	290	34.5	~3700
$[(NH_3)_5CoO_2Co(NH_3)_5]$	l.f. $^1A_1 \rightarrow \{^1E^a, {}^1A_2\}$	~450 (sh)	~22	--
$(NH_3)_4 \cdot 2H_2O$	$\pi^*(O_2^{2-}) \rightarrow d\sigma^*$	~360 (sh)	~27.8	--
Nujol mull, R.T.	$\pi^*(O_2^{2-}) \rightarrow d\sigma^*$	~310	~32.3	--
$[(NH_3)_5Co(O_2H)Co(NH_3)_5]$	l.f. $^1A_1 \rightarrow \{^1E^a, {}^1A_2\}$	~485	~20.6	--
$(HSO_4)_3SO_4)$	$\pi^*(O_2H^-) \rightarrow d\sigma^*(?)$	~360 (sh)	~27.8	--
Nujol mull, R.T.	$\pi^*(O_2H^-) \rightarrow d\sigma^*(?)$	~300	~33.3	--
$(CN)_5CoO_2Co(CN)_6^{6-}$	$\pi^*(O_2^{2-}) \rightarrow d_{z^2}(?)$	370 (sh)	27.0	5050
3N KOH, 0°C	$\pi^*(O_2^{2-}) \rightarrow d_{z_2}(?)$	314	31.8	10,000
$(CN)_5CoO_2H^{3-}$	l.f. $^1A_1 \rightarrow {}^1E^a$	370	27.0	280
2N KOH, 0°C	$\pi^*(O_2^{2-}) \rightarrow d_{z^2}$	272	36.8	4440

in the symmetry of the complex, the degeneracy of the O_2^{2-} π^* level is removed. A torsional angle of 90° would correspond to a minimum splitting of the π^* level, both components then being roughly equally σ bonding (each, crudely speaking, to a single Co(III)). Increasing the torsional angle should increase the π^* splitting, one component being σ non-bonding in the limit of 180°. We can thus expect two observed transitions in the present case of an angle of 146°, both transitions being $\sigma \rightarrow \sigma^*$ type transitions and being expected to have roughly equal intensity, as observed.

Two transitions at similar wavelengths, 357 nm and 277 nm, can be seen in a published spectrum[111] of an oxygenated Co(II) solution in aqueous ethylenediamine. The exact splitting of the two peaks is clearly expected to be a function of the other ligands in the complex and their steric properties, larger splittings being expected for more sterically hindered ligands and the resulting larger torsional angles. The somewhat larger splitting observed for the ethylenediamine complex is consistent with this rationale. An interesting example is the L-histidine complex,[112] $[Co(C_6H_8N_3O_2)_2]_2O_2 \cdot 3H_2O$, which has been reported to have a band at 385 nm ($\epsilon = 1620$), presumably assignable as the lower energy of the two charge-transfer transitions observed for the ammine complex. The rather bulky histidine ligands are expected to force a relatively large torsional angle. The intensity of the lower energy transition would, incidentally, be expected to decrease for

larger torsional angles, as the π^* derived level involved became less bonding.

The ligand-field portion of the spectrum shown in figure IV-1 is very poorly defined, with perhaps a poorly resolved shoulder being seen at ~500 nm ($\epsilon \simeq 500$). More concentrated aqueous solutions of the oxygen complex are rather difficult to investigate, higher O_2 pressures being necessary to avoid interference from the spectrum of Co(II) and decomposition reactions also being more important. The crystalline μ-peroxo dimer can be dissolved without rapid decomposition in several non-protic solvents (solutions in dimethylacetamide, in particular, show a charge-transfer spectrum similar to that of figure IV-1), but these solutions are very sensitive to traces of water and reliable data on the low-energy portion of the spectrum could not be obtained. Also, the conditions (high pressure and vacuum) involved in the preparation of KBr pellets, (the method of preference for the determination of solid state spectra) also seem to lead to partial reversal of the oxygenation reaction.

In figure IV-2 we show a Nujol mull spectrum of $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_4 \cdot 2H_2O$. We should comment that relative intensities in Nujol mull spectra are quite different from those in solution spectra, dispersion effects (among others) decreasing the observed intensities of strong peaks relative to weaker peaks.

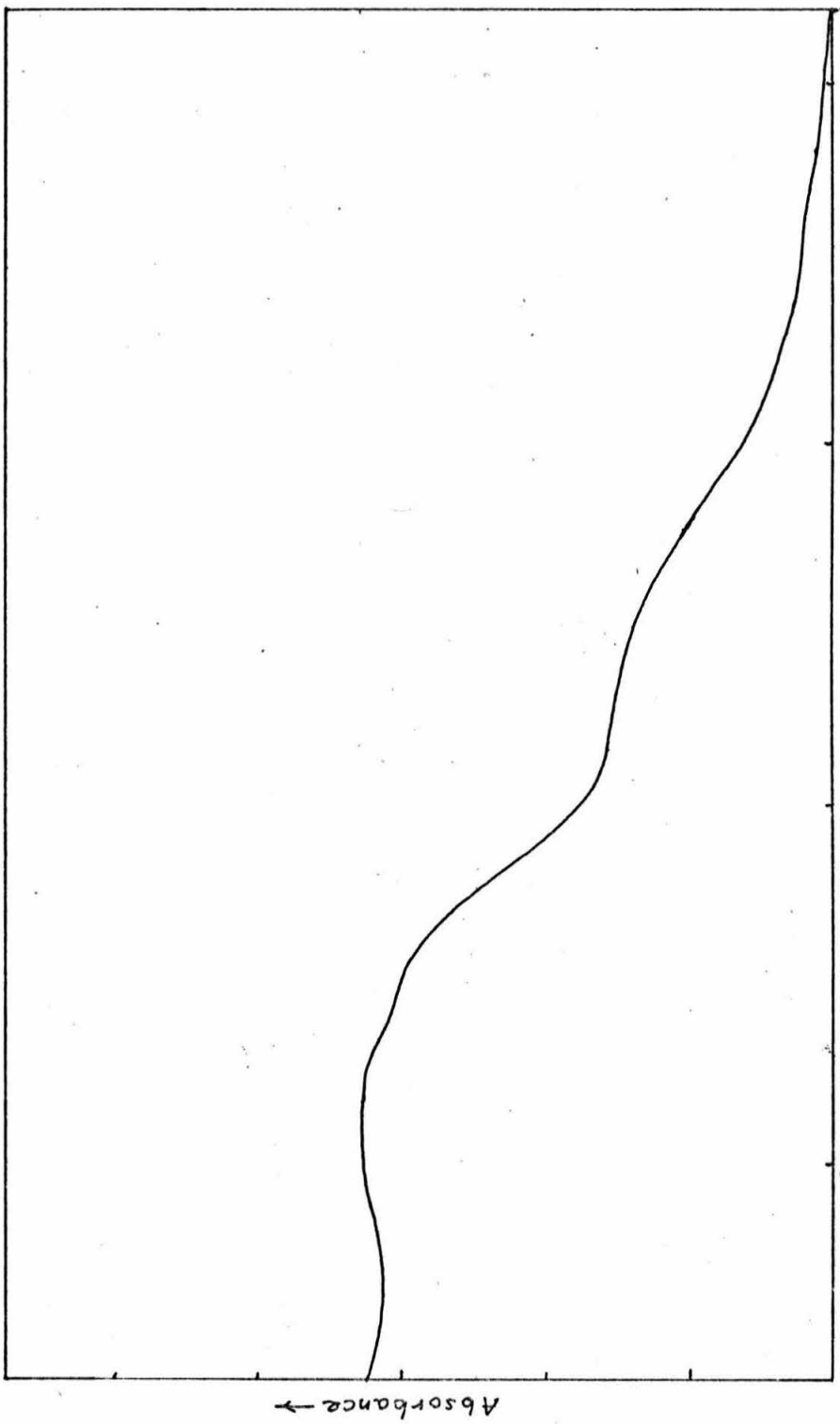


Figure IV-2. Electronic spectrum of nitrate salt of $(NH_3)_5CoO_2Co(NH_3)_5^{4+}$ as Nujol mull.

We observe two poorly defined peaks at ~310 nm and ~360 nm, corresponding to the two charge-transfer transitions observed in solution. In addition, we observe a fairly well defined shoulder at ~450 nm. We assign this as the "unsplit" $^1A_1 \rightarrow \{^1E^a, {}^1A_2\}$ Co(III) ligand-field transition. $Co(NH_3)_6^{3+}$ shows its $^1A_{1g} \rightarrow {}^1T_{1g}$ transition at 475 nm,[99] and the correspondence, considering the poor resolution of the mull spectrum, is rather good. We most definitely do not observe any lower energy transitions which might be assigned as $^1A_1 \rightarrow {}^1E^a$, and the intensity of the 450 nm shoulder indicates that this is in fact the lowest energy ligand-field transition. The correspondence to $Co(NH_3)_6^{3+}$ indicates that the ligand-field strength of the bridging O_2^{2-} is close to that of NH_3, more detailed conclusions clearly not being justified. We might specifically note that the true wavelength of the μ-peroxo transition is probably somewhat larger than 450 nm, because of the dispersion, etc. effects noted earlier.

A variety of μ-peroxo dimers with multidentate nitrogen bases, many of which are more stable than the ammine complex in solution, show[113] more or less well-resolved peaks at ~500 nm, with ϵ's on the order of 400, again assignable as the $^1A_1 \rightarrow \{^1E^a, {}^1A_2\}$ transition, the scatter in the values reflecting the scatter in the ligand field strength of the various bases. Fortunately, there exists one example of a nitrogen base μ-peroxodicobalt complex for which we can give a somewhat more detailed analysis of the ligand-field strength of O_2^{2-}. The μ-peroxo

complexes with the quadidentate ligand cyclam(1,4,8,11-tetraazacyclotetradecane), $[Co(cyclam)X]_2O_2^{n+}$, have been prepared by Tobe, et al. for various X, and their spectra reported.[114] Furthermore, a variety of derivatives trans-$Co(cyclam)X_2^{n+}$ have also been reported.[115] These trans-disubstituted complexes show large $d\sigma^*$ splitting (for reasons discussed in chapter 2) and thus have their lowest ligand-field band shifted well away from the charge transfer bands, and well resolved. The large number of derivatives reported allows detailed comparisons, and we derive a spectrochemical series $NH_3 > NCS^- > O_2^{2-} > OH_2$ from the reported spectra. (Quantitative treatment by the method of Wentworth and Piper[31] yields a Dq ordering NH_3 (2.5) > NCS^- (2.2) > O_2^{2-} (2.1) > OH_2 (1.9).) We do not feel that the high position of O_2^{2-} relative to OH_2 indicates that O_2^{2-} is a weaker π-donor (and therefore a very weak π-donor) but rather that it indicates that O_2^{2-} is a very strong σ-donor, at least comparable to NH_3, with π-donation decreasing its position in the spectrochemical series. (There should clearly be no strong correlation to OH_2, as the donor orbitals in the two ligands are fundamentally different.) The ligand field spectra, of course, give no direct information on this point, but comparison to μ-O_2^- complexes (vide infra) is suggestive in this regard.

The μ-O_2^{2-} complexes protonate in acidic solution, and evidence has been presented[101] for two protonated forms of the

well-studied di-bridged complex $(en)_2Co\text{-}\mu(NH_2, O_2)\text{-}Co(en)_2^{3+}$, a labile orange form with the structure of the O_2 bridge presumably unchanged, and a rearranged red form, reverting to the parent complex rather slowly in basic solution. The crystal structure of the red form has been determined,[117] and shows both cobalt centers bound to a single oxygen of the hydroperoxide ion. The O_2 unit lies at an angle of 41° out of the CoNCoO plane, with a CoOCo angle of 101°. We could naively look at the bonding in this unit as being rather similar to that in the $\mu\text{-}O_2^{2-}$ complex, each component of the O_2^{2-} π^* level again being involved in σ donor interaction with one Co(III). The bonding of the proton, of course, somewhat complicates this simple picture. It is not at all clear in the case of a bound proton that the interaction can be described only in terms of O_2^{2-} π^* orbitals, although the very close similarity of the O-O distances in O_2^{2-} and H_2O_2 (1.49 Å versus 1.48 Å[119]) would seem to imply that the bonding in the O_2 unit is not greatly changed, and that the O-H bond can be taken as a relatively weak perturbation on the electronic structure. Granted this, the π^* levels in O_2H^- should still be decidedly non-degenerate.

In figure IV-3 we show the electronic spectrum of the sulfate salt of $(NH_3)_5Co(O_2H)Co(NH_3)_5^{5+}$ in Nujol mull. This red salt is prepared by treating the μ-peroxo complex with 3N sulfuric acid, and is stable only as a solid, having transitory existence in aqueous solution. We assume this salt to have a structure analogous to the one discussed above.

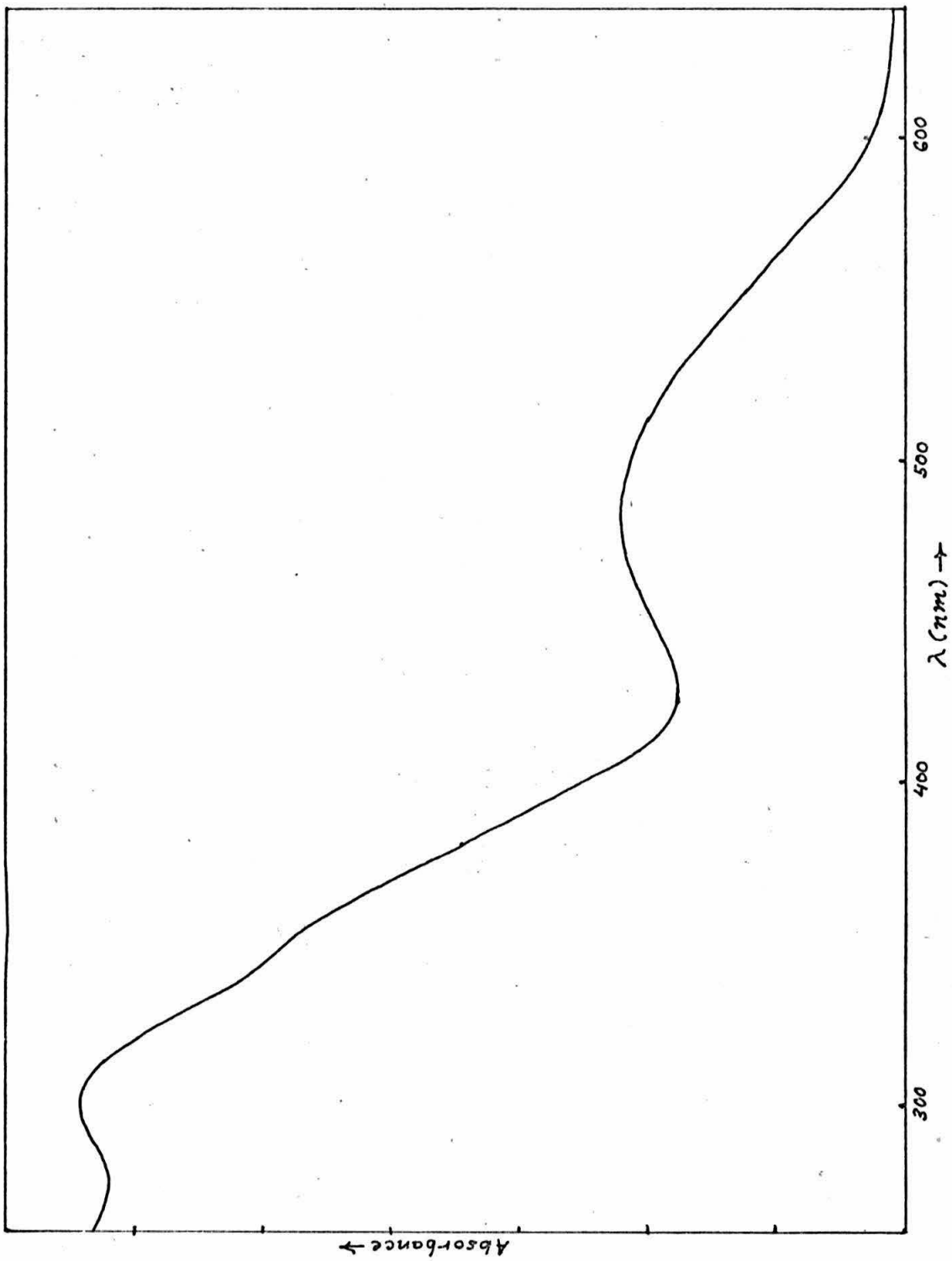


Figure IV-3. Electronic spectrum of sulfate salt of $(NH_3)_5Co(O_2H)Co(NH_3)_5^{5+}$ as Nujol mull.

Rather surprisingly, the charge transfer spectrum is qualitatively similar to that of the μ-peroxo complex, showing a maximum at $\sim$300 nm and a shoulder at $\sim$360 nm. The ligand field spectrum is distinctly changed, however. (As is, of course, more simply indicated by the red color of the compound, versus the yellow-brown color of the μ-peroxo complex.) A well-resolved peak is seen with a maximum at $\sim$485 nm, shifted to lower energy from the μ-peroxo peak. This complex has been detected as a transitory species in solution[118] and a peak at $\sim$500 nm has been identified, with the ϵ being estimated to be $\sim$200.[118] (The difference in wavelength between the solution maximum and the solid state maximum is, again, probably due to the Nujol mull technique rather than to a real solid state shift.) The bridging O_2H^- ligand in this complex thus seems to have a ligand field strength close to that of H_2O. The reduction in ligand field strength from μ-O_2^{2-} is logically explained by the formation of an O-H bond, less π^* electron density then being available for sigma donation to the metal ions.

The charge transfer maximum at 300 nm seems to indicate that at least one of the π^* levels is not greatly perturbed from its energy in the μ-peroxo complex. Since we have no information on the true intensities of these peaks (relative and/or absolute), we refrain from comment on the shoulder at 360 nm. Clearly, a $Co(NH_3)_5O_2H^{2+}$ monomer would provide a better comparison to the μ-peroxo complex, but, unfortunately, the monomer has never been isolated.

The cyanide analogue of the μ-peroxodecaammine, $(CN)_5CoO_2Co(CN)_5^{6-}$, is also a long-known species, but remains much less well characterized. The potassium salt is reported to be diamagnetic,[120] but no crystal structure has been done. The ion is only stable with respect to hydrolysis at extremely high pH's in solution. In contrast to the ammine system, the oxygenation of $Co(CN)_5^{3-}$ seems to be completely irreversible,[103] with the decomposition of the ion giving a stoichiometric amount of hydrogen peroxide. In further contrast, the mononuclear $Co(CN)_5O_2^{3-}$ has been detected as an intermediate in aqueous solution.[121]

In figure IV-4 we show the electronic spectrum of $(CN)_5CoO_2Co(CN)_5^{6-}$ in 3 N KOH. The spectrum shows only a broad peak at 314 nm (ϵ = 10,100) and a broad shoulder at ~ 370 nm (ϵ ~ 5000). A weak peak observed at ~ 500 nm does <u>not</u> correspond to the μ-peroxo complex, but rather to its oxidation product, $(CN)_5CoO_2Co(CN)_5^{5-}$, and the relative intensity of this peak is a function of sample, mixing conditions, and time. The exact wavelength of the major μ-peroxo transition's maximum also varied from sample to sample, which is a result of the presence of hydrolysis and oxidation products.

We also show, in figure IV-5, a KBr pellet spectrum of $K_6[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$, the spectrum being very similar to the solution spectrum, which at least establishes the similarity of the species in the solid and in solution. (The relative intensities for a KBr pellet spectrum are rather more believable than those

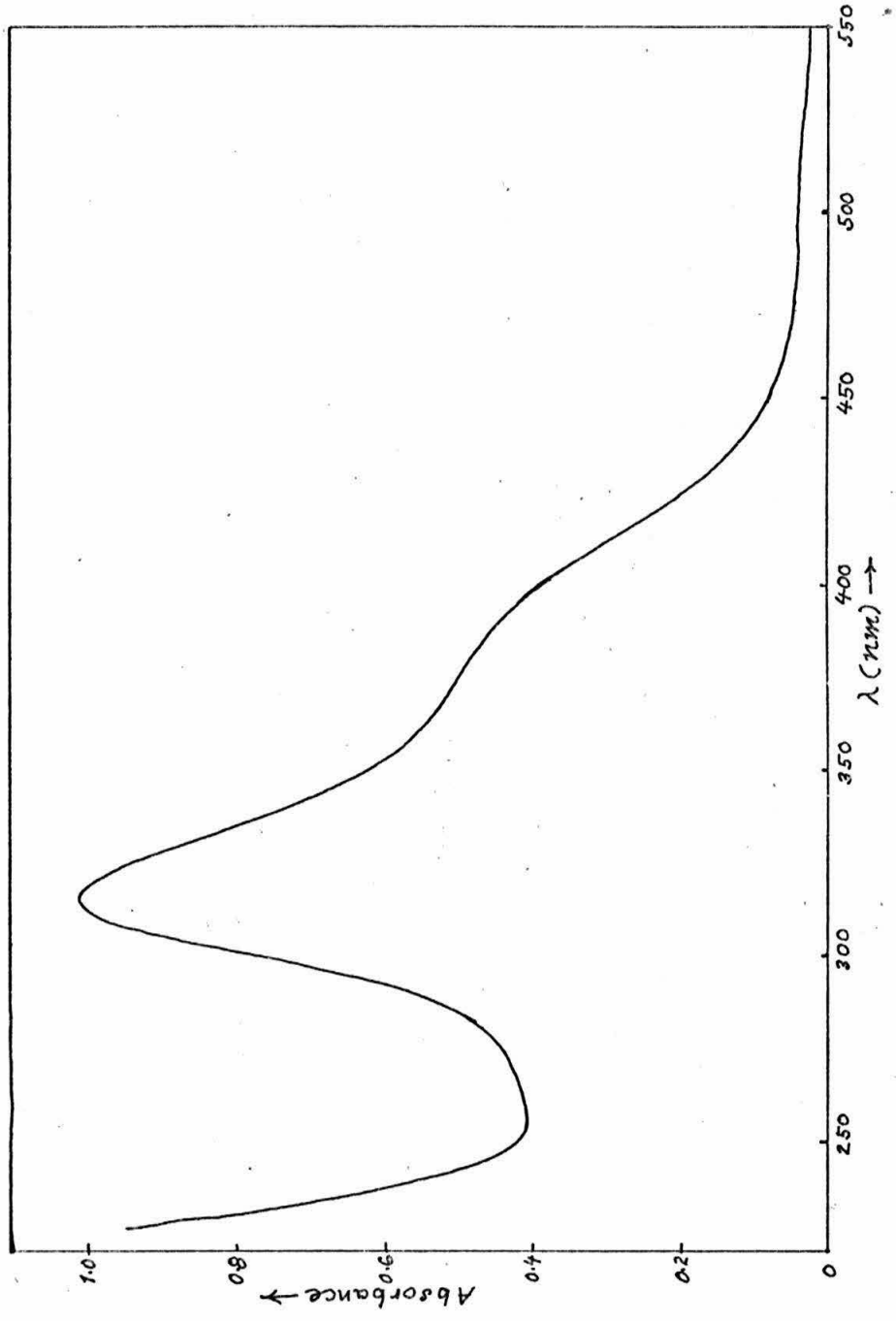


Figure IV-4. Electronic spectrum of $(CN)_5CoO_2Co(CN)_5^{6-}$, 10^{-4} M in 3M KOH at 0 °C.

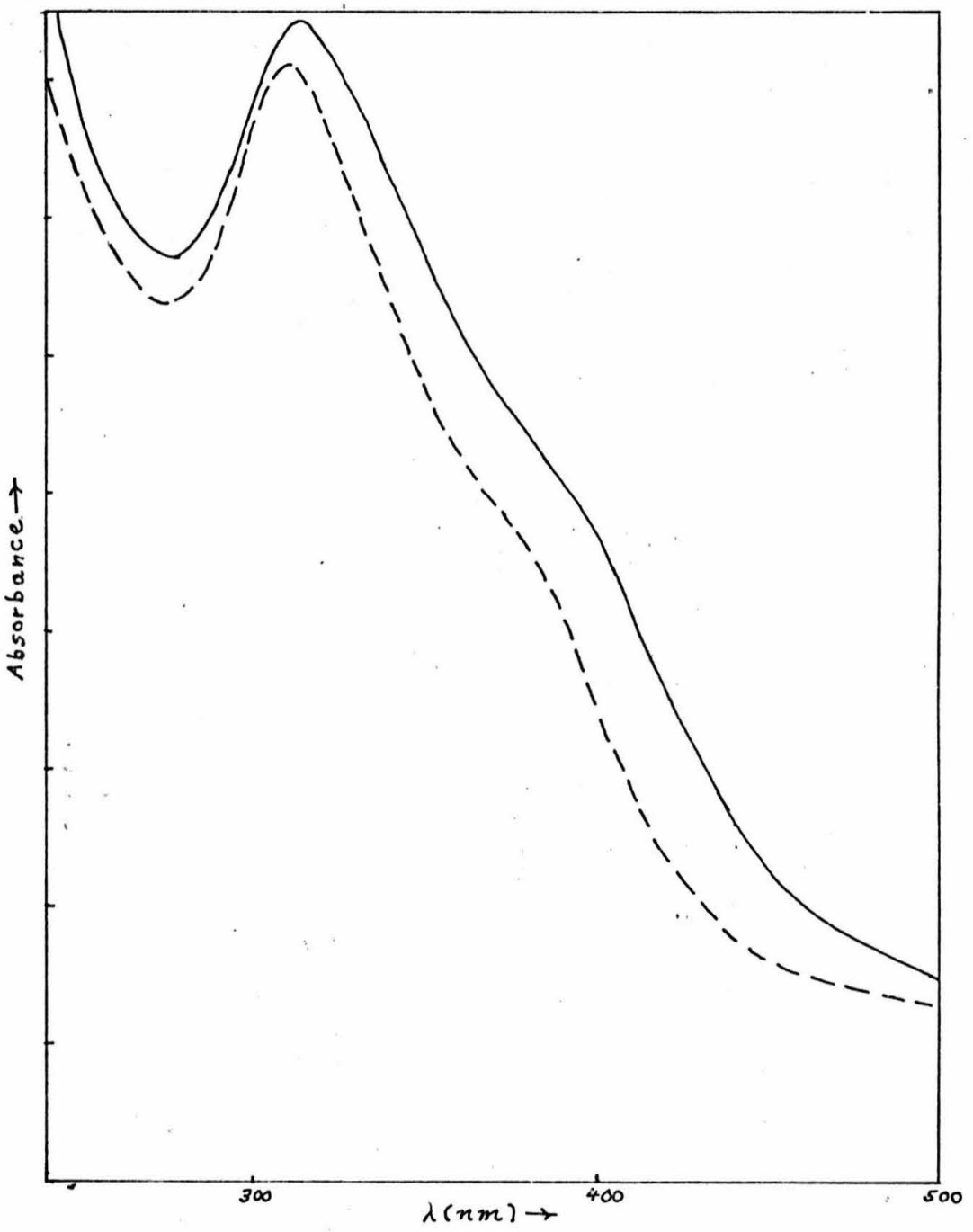


Figure IV-5. Electronic spectra of $K_6[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$ dispersed in KBr at R. T. (——) and 78°K (----).

of a Nujol spectrum, the major deviation from ideality for a well-prepared pellet being the superposition of a moderate scattering curve.) We also observe the presence of some μ-superoxo impurity in the solid, and have observed variable amounts of the μ-superoxide in all of the samples we have prepared.

As to assigning the observed spectrum, we would assign the peak at 314 nm and the shoulder at 370 nm to the split transition $\pi^*(O_2^{2-}) \rightarrow d_{z^2}$, the two components being ascribed to the two split components of the O_2^{2-} π^* levelas for the decaammine. The shoulder at 370 nm is at roughly the right wavelength to be the expected $^1A_1 \rightarrow {}^1E^a$ ligand field transition, but seems far too intense to be this transition, and the ligand field band is probably buried underneath. For the cyanide complex, we expect a large splitting of the $d\sigma^*$ orbitals, hence the assignment as transitions to d_{z^2}. Transitions to $d_{x^2-y^2}$ are expected between 250 and 300 nm, and as these are expected to be weaker than the transitions to d_{z^2}, and easily unobservable, we cannot say for certain whether the observed spectrum fits our expectations or not. (The apparent shift of the charge transfer bands to lower energy going from NH_3 to CN^- is rationalizable on the above grounds, with the transition to $d_{x^2-y^2}$ being a better indication of the increase in Δ, if observed.)

Given the low resolution of the spectrum, and the additional uncertainty introduced by the extreme difficulty of obtaining the complex in a pure state, the assignments cannot be regarded as

being exceptionally convincing. Additionally, the formulation of the complex as a μ-peroxo dimer is not at all confirmed, and some unexplained anomalies cast some doubt on the formulation. The solid state infrared spectrum of the complex, as both the potassium and barium salts, shows at least four sharp bands in the ν(CN) region, with the metal-cyanide stretches and bends being similarly complex. Furthermore, the electronic spectrum of a complex reported[122] to be $Co(CN)_5O_2^{3-}$, a superoxide monomer, is remarkably similar to the spectrum of the dimer (vide infra). We will therefore expend no further effort in "explaining" the spectrum.

In moderately acidic solution, a protonated form of the dimer with an absorption maximum at ~ 300 nm is produced, the spectrum reverting to the original spectrum on addition of alkali if the solution is not allowed to stand very long. The protonated species might be analogous to the μ-hydroperoxodecaammine complex. On standing, the dimer irreversibly hydrolyzes, with the $Co(CN)_5O_2H^{3-}$ ion being produced as a primary product. This complex is isolable,[104,123] and seems to be well-behaved. It is a very weak acid, showing no spectral changes between pH 7 and 12,[123] hence we will discuss the spectrum in terms of a hydroperoxide formulation (which is also indicated by the infrared spectra of solid salts[104]).

The complex shows a well-resolved ligand field band at 370 nm (ϵ = 280), assignable as $^1A_1 \rightarrow {}^1E^a$. The ligand-field

strength of the O_2H^- ligand is thus seen to be relatively close to, and slightly greater than, that of OH_2 (c.f. chapter 2). The lowest charge transfer transition is observed at 272 nm (ϵ = 4440). Investigation of lower wavelengths is difficult because of the necessity to maintain the complex in basic solution, which has a cut-off near 230 nm. However, within this limitation, no other charge transfer bands are seen. (Although the 272 nm peak shows a sharp maximum, the peak is shouldered on rising high-energy absorption, and weak peaks to higher energy would be unobserved.)

The 272 nm peak is readily assigned as $\pi^*(O_2H^-) \rightarrow d_{z^2}$. That two peaks are not observed would seem to indicate that in this complex at least, interaction of the proton has greatly split the π^* level, and we see a transition from only one component, presumably the one which is bonding to the Co(III). (A weak transition to $d_{x^2-y^2}$ would be expected at $\sim$ 230 nm, with non-observance not being very surprising.)

If we accept as valid the charge-transfer energies we found for $(CN)_5CoO_2Co(CN)_5^{6-}$, we would conclude that replacement of a pentacyanocobalt(III) unit by a proton causes a large increase in the energy of $\pi^*(O_2^{2-}) \rightarrow d\sigma^*$ charge transfer. This effect can be explained by a crude argument invoking the repulsion of the filled Co(III) $d\pi$ orbitals with the filled π^* levels, leading to a net stabilization of both π^* levels in the hydroperoxide complex over those of the μ-peroxo dimer.

As this section has presented a mixture of "believable" and "not necessarily believable" results, it seems worth while to summarize those points we feel to be reliably established.

The ligand field strength of the complexed peroxide ion is slightly less than that of N-bound thiocyanate, and considerably greater than that of water. Protonation of the peroxide group decreases the ligand field strength, although it remains somewhat greater than that of water. Charge transfer bands are observed at energies roughly comparable to those observed for Br^- π charge transfer, with two split components being observed for μ-O_2^{2-} complexes, corresponding to the two π^* components in the low symmetry of the complexes. Somewhat more tentatively, we also conclude that protonated peroxide complexes show charge transfer bands shifted to higher energy, with monomeric hydroperoxides showing a single charge transfer band at energies more comparable to that of azide or thiocyanate charge transfer.

Co(III) Superoxide Complexes

The $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$ ion, which we will refer to in this section as the "decaammine", can now be confidently formulated as a μ-superoxo dicobalt(III) ion. Fundamental to this state of affairs is the accurate structural determination by Schaefer and Marsh[98] of the sulfate tris(bisulfate) salt, which revealed a cation with an O-O distance of 1.31 Å, to be compared to that of 1.28 Å found in alkali superoxides, and Co-N distances typical of Co(III) complexes rather than Co(II) (for example) complexes. The cation

shows a planar Co-O-O-Co unit, with a Co-O-O angle of 118°, and with the projection of the O_2 unit into the CoN_4 planes being directed at 45° to the N-Co-N axes. The entire cation has a symmetry very close to C_{2h}.

Electron spin-resonance results are consistent with the crystal structure, showing the equivalence of the cobalt atoms from the ^{59}Co hyperfine structure.[125] Furthermore, the ^{17}O hyperfine splitting observed in a ^{17}O substituted complex,[126] comparable to that of O_2^-, as well as the magnitude of the cobalt hyperfine constant,[125] indicate a very high residence time of the unpaired electron on the O_2 bridge, and correspondingly very low delocalization into cobalt orbitals.

The $(CN)_5CoO_2Co(CN)_5^{5-}$ ion (which we will refer to as the "decacyanide") is the cyanide analogue of the decaammine. For the decacyanide, we have no crystal structure to establish the geometry of the anion. The only salt which we found to crystallize well is the potassium salt, and this salt, unfortunately, has a very strong tendency to form branching dendrites rather than single large crystals. (The dendrites do show strong polarizations under a polarizing microscope, establishing their crystallinity.) However, the infrared spectrum of the salt is characteristic of a pentacyanocobaltate(III) complex, and a e.s.r study[102] showed the decacyanide to have a g value and ^{59}Co hyperfine structure very similar to that of the decaammine, with a slightly smaller A_{Co}

indicating an electron perhaps even more localized on the superoxide bridge. We thus feel confident in formulating this complex as a μ-superoxodicobalt(III) complex, and infer a geometric structure similar to that of the decaammine, particularly in view of the bridge localized unpaired electron. (We will justify this point in the succeeding discussion.)

In figures IV-6 and IV-7, we show the solution electronic spectrum of the decaammine ion at room temperature and 77°K. In figure IV-8 we show the solution electronic spectrum of the decacyanide ion at room temperature and 77°K, while in figure IV-9 we show the KBr pellet spectrum of the potassium salt, which we include primarily to show the identity of the electronic spectrum in solution and in the solid (and, therefore, the integrity of the ion in solution.)

Probably the most prominent feature of the decaammine spectrum is the low energy peak at ~15 kK (which makes the compound blue-green in solution and in the crystal) but we will defer discussion of this peak for the moment, and consider the peaks in the spectrum which can clearly be assigned as ligand-field in origin.

$Co(NH_3)_6^{3+}$ shows its ligand field transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ at 21.05 kK (ϵ = 60) and 29.50 kK (ϵ = 55), respectively.[99] In the spectrum of the decaammine, we find a peak at 20.83 kK (ϵ = 305), showing a definite blue-shift and decrease in integrated intensity at 77°K, and also a shoulder at

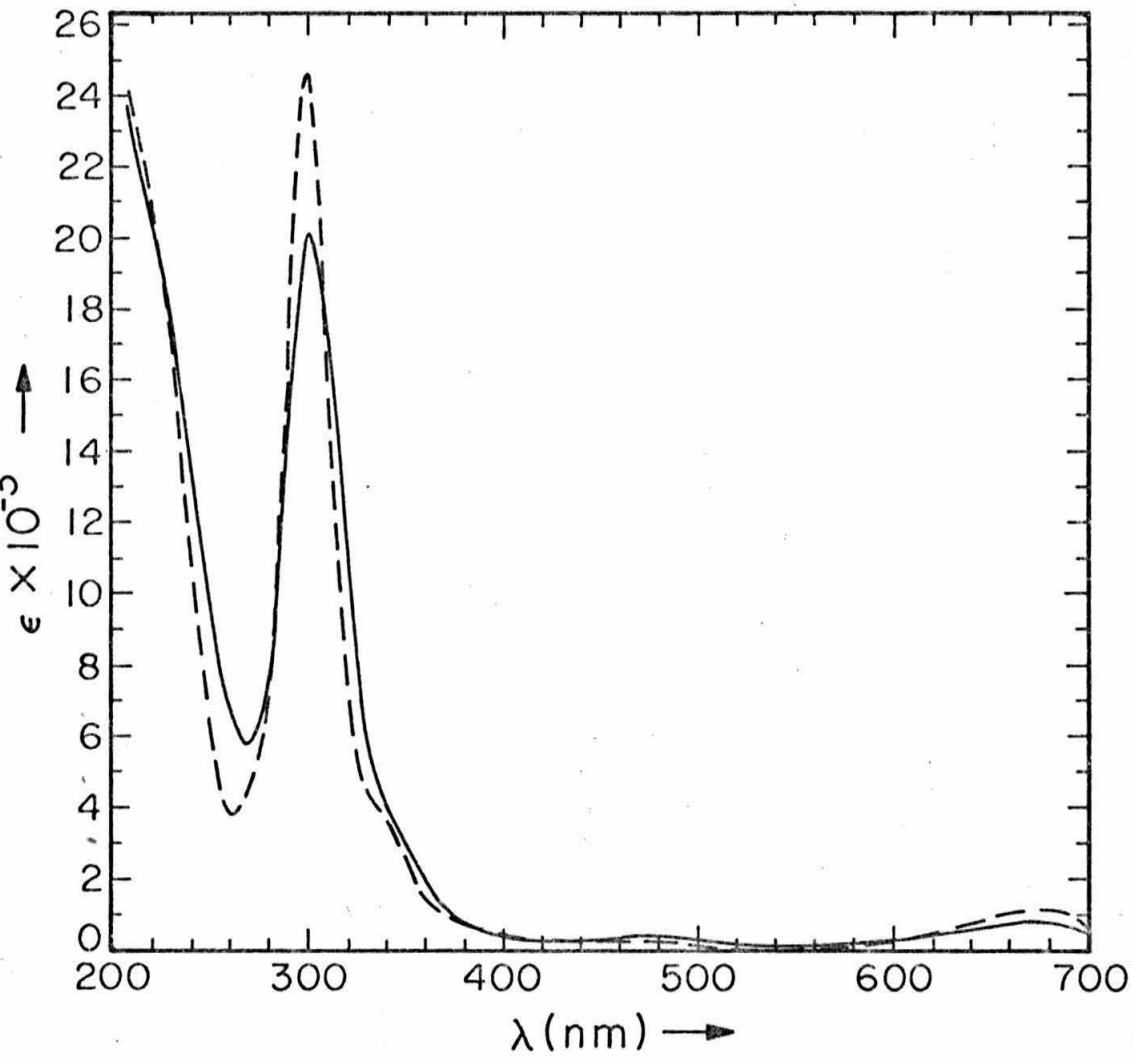
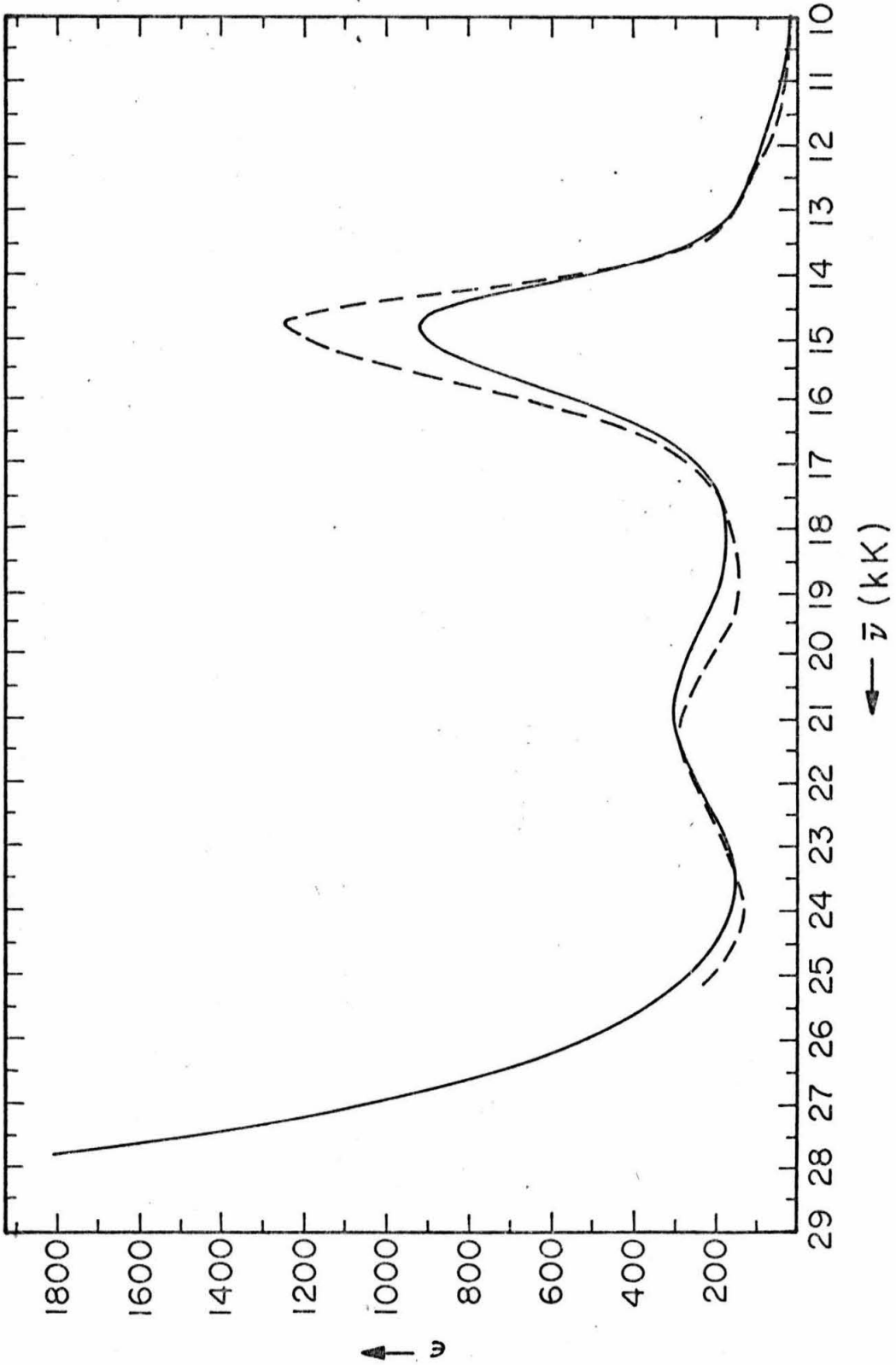


Figure IV-6. Electronic spectra of $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$ in 50% saturated aqueous LiCl at R.T. (——) and 78°K (----).

Figure IV-7. Electronic spectra of $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$ in 50% saturated aqueous LiCl at R.T. (——) and 78°K (----).


1800
1600
1400
1200
1000
800
600
400
200
ε
29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10
$\bar{\nu}$ (kK)

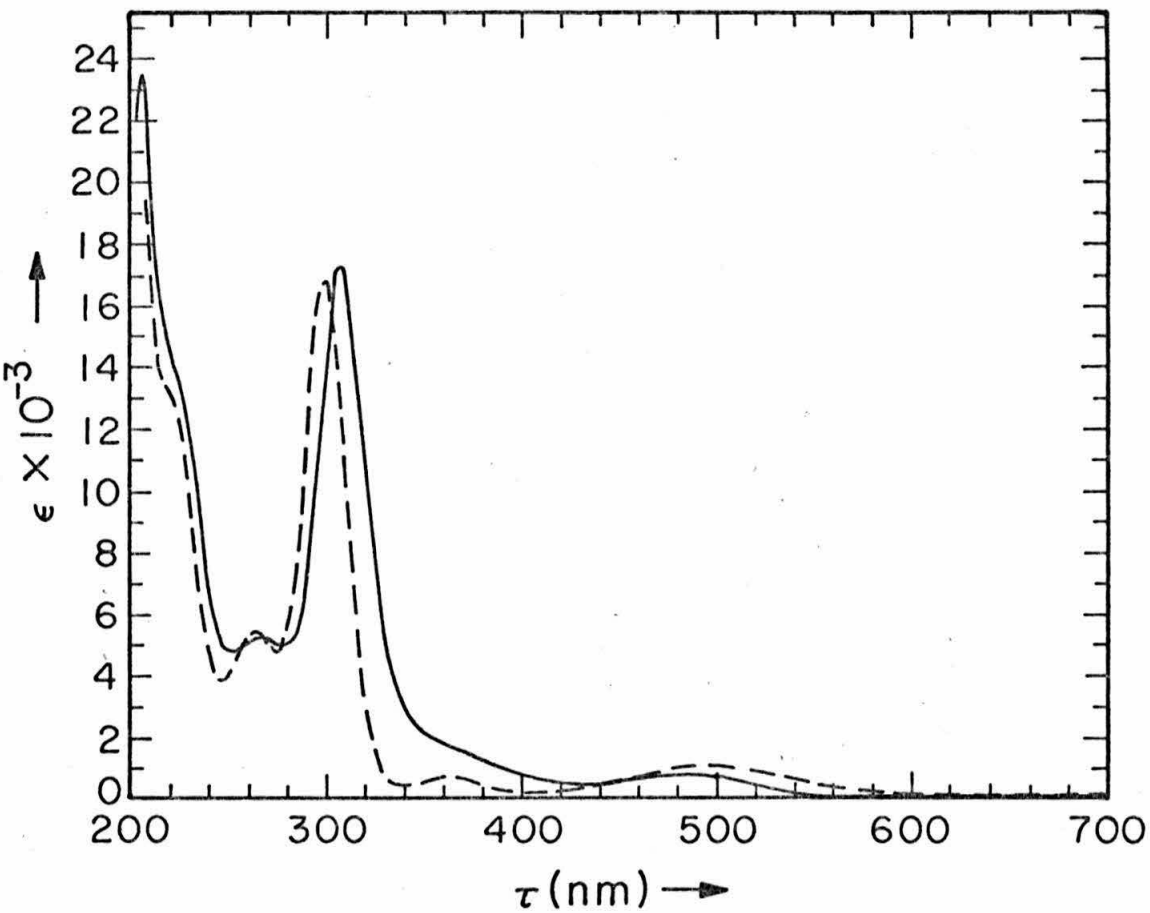


Figure IV-8. Electronic spectra of $(CN)_5CoO_2Co(CN)_5^{5-}$ in 50% saturated aqueous LiCl at R.T. (——) and 78°K (----).

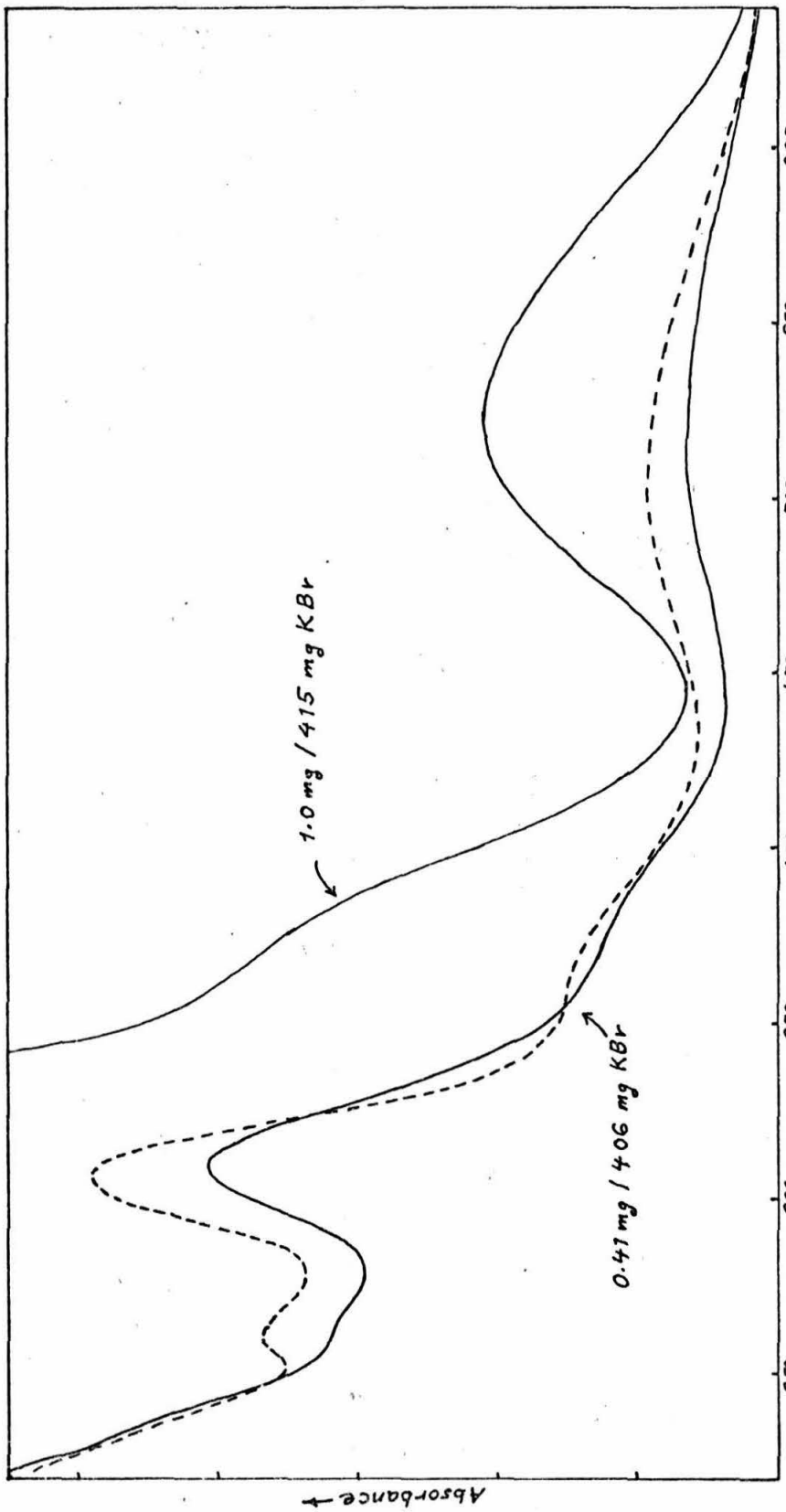


Figure IV-9. Electronic spectrum of $K_5[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$ dispersed in KBr at room temperature (——) and 78 °K (----).

Table IV-2

Electronic Spectra of μ-Superoxodicobalt Complexes

	300°K			77°K		
	λ_{max}(nm)	ν_{max}(kK)	ϵ	λ_{max}(nm)	ν_{max}(kK)	ϵ
$[(NH_3)_5Co)_2O_2]Cl_5 \cdot 4H_2O$	~800 (sh)	~12.5	~ 110	~790 (sh)	~12.7	~ 130
in	671.5	14.89	927	675.5	14.80	1249
1:1 saturated LiCl:1M HCl	480	20.83	309	472.0	21.19	291
	~345 (sh)	~28.9	~ 3,450	~342 (sh)	~29.2	~ 3,460
	302	33.1	20,160	301	33.2	23,960
$K_5[(CN)_5Co)_2O_2] \cdot H_2O$	812	12.3	14	--	--	--
in	485.5	20.59	745	491.0	20.35	1,120
1:1 saturated LiCl:H_2O	~373 (sh)	~26.8	~ 1,500	362	27.65	670
	310.5	32.20	17,250	301.5	33.16	16,750
	268	37.71	5,230	266	37.59	5,440
	~225 (sh)	~44.4	~13,800	~225 (sh)	~44.4	~12,800
	208	48.07	23,540	--	--	--

$\sim$29 kK ($\epsilon \sim$ 3500), showing a much improved resolution at 77°K. The intensity of the lower-energy transition is not very abnormally high for a ligand-field transition in a substituted complex, while the true intensity of the 29 kK peak is clearly much less than the observed peak ϵ, and we feel confident in assigning these peaks as ligand-field transitions, particularly in view of the close correspondence to the hexaammine values.

The intensity of the 20.83 kK peak would seem enormously high if this were the $^1A_1 \rightarrow {}^1A_2$ transition. Furthermore, if we nevertheless assign this peak as $^1A_1 \rightarrow {}^1A_2$, we must necessarily assign the (again, rather too intense) 14.9 kK peak as the $^1A_1 \rightarrow {}^1E^a$ transition, and such an assignment would give unacceptably high values of Dt (implying Dq $(O_2^-) < 0$). With such an assignment, of course, the close energy correspondence of the 29 kK band to the hexaammine $^1A_1 \rightarrow {}^1T_{2g}$ transition then also becomes difficult to explain.

Avoiding such paradoxes, we assign the 20.83 kK peak as the "unsplit" $^1A_1 \rightarrow \{{}^1E^a, {}^1A_2\}$ transition. The very slight shift of this transition from $Co(NH_3)_6^{3+}$ implies that $Dq(NH_3) \simeq Dq(O_2^-)$, that is, that O_2^- is a moderately high field ligand. The 29 kK peak can then be assigned as the $^1A_1 \rightarrow \{{}^1E^b, {}^1B_2\}$ transition, with the difference in energy between the two transitions (16B) giving $B \simeq 510\ cm^{-1}$, to be compared with $B = 530\ cm^{-1}$ for $Co(NH_3)_6^{3+}$.[31] We thus further conclude that the "nephelauxetic effect" of O_2^- is

comparable to that of NH_3 and that O_2^- seems on these ground to simply be a strong σ donor.

Turning to the spectrum of the decacyanide, we observe a peak at 362 nm (at 77°K), showing a large decrease in intensity from room temperature to 77°K (from $\epsilon \simeq 1500$, shouldered, to $\epsilon \simeq 670$.) We assign this peak as the $^1A_1 \rightarrow {}^1E^a$ transition. The wavelength may be compared to that of $Co(CN)_5NH_3^{2-}$, 345 nm,[37] and also that of $Co(CN)_5NCS^{3-}$, 363 nm.[35] We conclude that O_2^- is a slightly weaker field ligand than NH_3, very comparable to N-bonded thiocyanate. This is quite consistent with the unsplit ligand field band observed for the decaammine.

Yamada[127] has reported that, for the nitrate salt of the decaammine, the 20.8 kK peak is essentially non-polarized in single crystal spectra, while the 14.9 kK peak is very strongly polarized, and we have confirmed these measurements for the sulfate tris(bisulfate) salt, of known crystal structure, finding the 14.9 kK peak to be roughly polarized $||$ to the O-O bond. The lack of polarization of the 20.8 kK peak can be taken as further support for our ligand-field assignments, as an "unsplit" transition is not expected to show strong polarization (whereas a $^1A_1 \rightarrow {}^1A_2$ transition, for example, would be expected to be polarized). The polarization of the low-energy peak provides an important piece of information, very useful in the assignment of this peak.

In figure IV-10, we show an approximate molecular orbital diagram for the complex, assuming C_{2h} symmetry. The quantitative

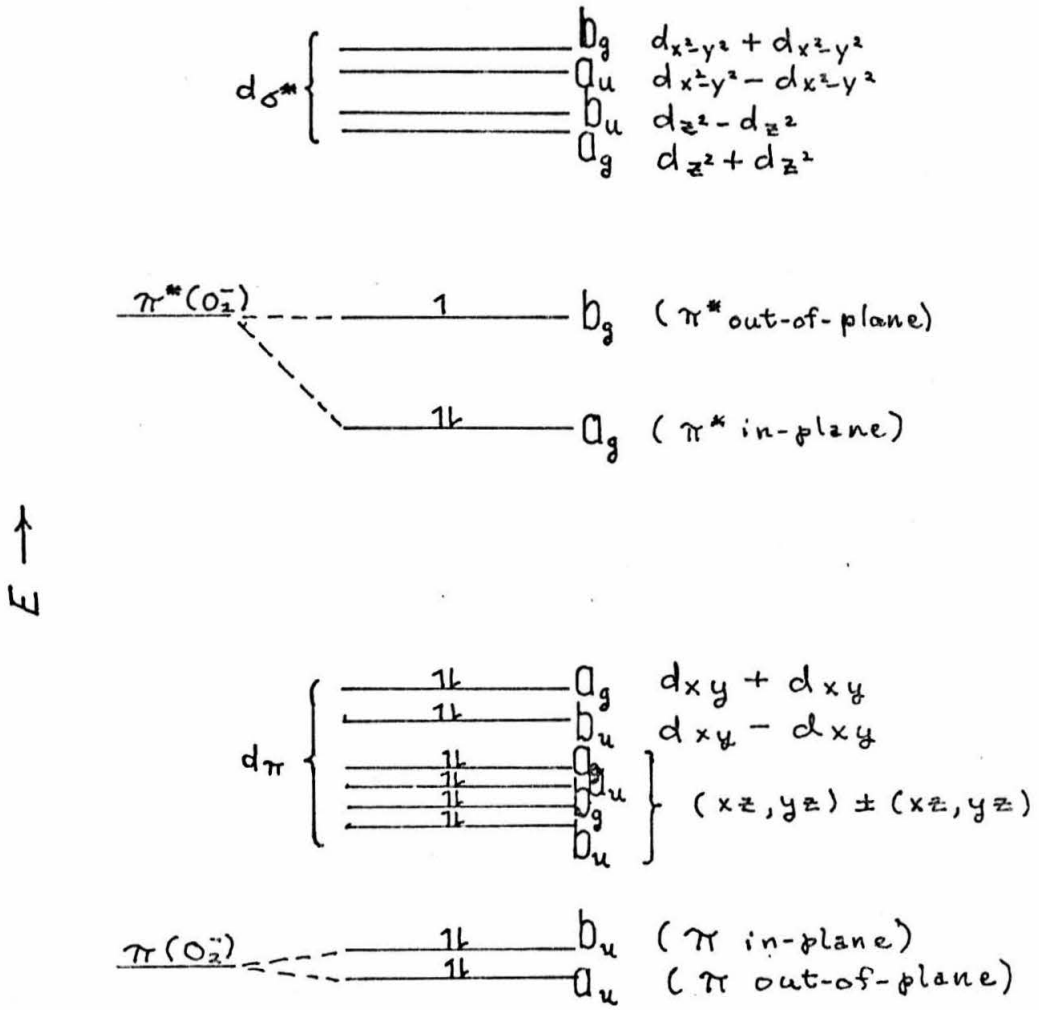


Figure IV-10. Molecular orbital diagram for a superoxide-bridged Co(III) dimer.

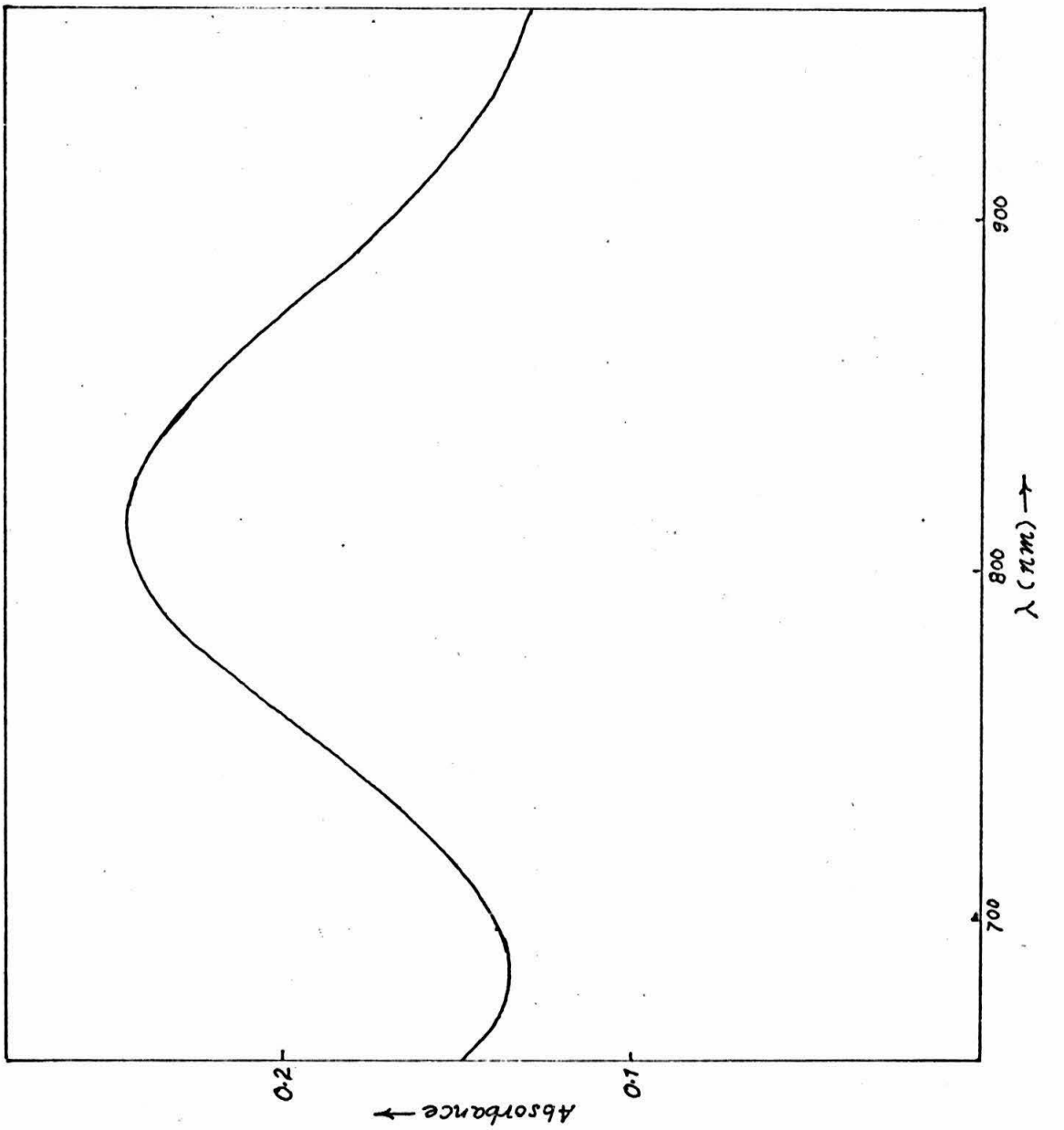


Figure IV-11. Electronic spectrum of $(CN)_5CoO_2Co(CN)_5^{5-}$ in the near-infrared, 10^{-3} M in H_2O, 10 cm pathlength.

predictive value of such a diagram is, of course, nil, and the relative energies of the various levels in the diagram have no great significance. The π^* level has been positioned so as to cater to the natural (although not necessarily justified, without information on relative values of spin-pairing energies) prejudice towards placing a level with an unpaired spin as the highest occupied level on an energy scale. Several comments on the diagram are in order.

We label the d orbitals according to their symmetry combinations in C_{2h} symmetry. We must strongly emphasize, however, that, as implied by the ligand-field spectrum, the metal ions in this complex are very weakly interacting (a situation quite typical of first-row transition elements, especially those lacking $d\pi$ holes and the resultant capacity for strong direct or ligand mediated π-interactions) and that the fully delocalized M.O.'s are therefore a rather poor description of the system. (This can be related to the improper dissociation limits of Hartree-Fock wave functions.) In particular, while the full symmetry of the cation is very important for consideration of transitions "localized" on the bridging O_2^- ligand, transitions involving the metal ions are undoubtedly <u>not</u> well described by transitions involving M.O.'s delocalized onto the two metal ions--ligand field transitions, for example, will not give excited states with equivalent cobalt atoms when they are very weakly interacting. This is equivalent to saying that the C_2 axis (and the inversion center generated by $C_2 x \sigma_h$)

is irrelevant to metal-involved transitions in this complex. The σ_h symmetry element, on the other hand, does not mix metal centers, and is quite relevant. In our subsequent discussion of group theoretical selection rules we will therefore primarily consider this symmetry element, while we will retain the C_{2h} state designations for labeling purposes. (The effect of the C_2 axis is to split d-levels into gerade and ungerade levels, as shown in figure IV-3. Taking these levels seriously, we find that only the gerade combinations can bond with the $O_2^- \pi^*$ levels, whereas only transitions from or to ungerade combinations are LaPorte allowed, which would lead to the prediction that no such charge-transfer transitions should be very intense,at complete variance with the observed spectrum. Looking at "localized" metal ions, of course, we simply merge the a_g, b_u, and b_g, a_u pairs to form 2a′ and 2a″ C_s levels. Selection rules arrived at in C_{2h} symmetry, incidentally, carry over into C_s symmetry.)

We can also ask whether the lack of distinguishability of x and y in C_{2h} symmetry (and also in C_s) is realistic. Group theoretical selection rules here actually do <u>not</u> provide for transitions polarized along the O_2 bond, but only for transitions polarized along the C_2 axis or perpendicular to this axis. In the C_{4v} microsymmetry of the metal ion, those metal O_2^- transitions being "x, y" polarized in C_{2h} would be polarized along the z-axis of the metal ion, this being a <u>very</u> distinguishable axis in C_{4v},

hence, roughly, along the O_2 axis. Here, we are simply noting that the σ_h plane introduced by the O_2^- ion is a relatively weak perturbation on the Co(III) ion. On the hand, it is not at all a weak perturbation on the O_2^- ion, and C_s ("C_{2h}") selection rules for metal O_2^- transitions should be valid, given that we read (x,y)-polarized as metal ion z-axis polarized.

For the O_2^- ion, we show the π^* orbitals, degenerate in the free ion, as strongly split in the complex. The π^* in-plane (the M-O-O-M plane) orbital is a σ-bonding orbital (primarily with the Co(III) d_{z^2}), and the π^* out-of-plane orbital is a primarily non-bonding orbital. This latter orbital can only bond to the metal ions in a π-fashion, with specification of the interaction as being π-donor or π-acceptor being rather meaningless for a half-filled orbital. The magnitude of such interaction (with the b_g $d\pi$ orbital, in C_{2h}) is difficult to predict, but would certainly be very much smaller than the strong σ interaction of the in-plane orbital. (It would incidentally be expected to increase the energy of the b_g π^* orbital. Certainly this interaction could not be very large or the ion would be easily oxidizable, which is not observed.) The primarily non-bonding nature of the half-filled orbital in our M.O. scheme provides insight into the e.s.r. results, with such delocalization of the unpaired electron into metal orbitals as is observed being due to π interactions. The non-bonding nature of the half-filled orbital is a result of the planar geometry, and we can thus infer such a geometry for the decacyanide, as noted earlier.

In explanation of the adoption of this geometry, we can argue from several viewpoints. Starting with the noninteracting $p_{x,y}$ orbitals of the oxygen atoms, it can be argued that the (hypothetical) ion $H_2O_2^+$ would be planar, because three electrons in a bonding-antibonding orbital pair gives net bonding. (For H_2O_2, a similar argument leads to the prediction that the molecule will be skewed, as observed, in order to create two "lone pairs" and avoid the net antibonding resulting from full occupation of a bonding-antibonding π orbital pair.[21]) A similar (but much less transparent) argument can be made from the (preferred) viewpoint of metal ions interacting with the π^* orbitals. We can additionally argue that repulsion of the filled metal $d\pi$ orbitals is clearly less with the half-filled π^* orbital than it would be with the filled π^* orbital, which should also contribute to stabilization of the observed geometry.

The bonding in the CoO_2Co unit corresponds to a 4 center 2 electron bond (or three center, if we take the O_2 as a single center). Multicenter bonding is certainly not unknown in inorganic chemistry at this stage, but the proposition of such a bond still seems somewhat unusual and worthy of comment. As previously noted, the $H_2O_2^+$ ion is indeed hypothetical, and HO_2 is the only protonated superoxide species which has been detected.[18,20] (However, protonation of monomeric metal-superoxide complexes and dissociation of hydroperoxide is probably one of the more common autoxidation mechanisms.[128]) It should be emphasized

that the μ-superoxo complexes are not prepared by nucleophilic substitution, but by oxidation of μ-peroxo complexes, so that the M-O_2-M unit is "pre-formed." It may well be that much of the stability of the μ-superoxo complexes is simply due to the absence of an energetically favorable decomposition process, dissociation of a Co(II) (as for the μ-peroxodecaammine) not being possible because it would leave a Co(III) dioxygen complex, and proton-assisted decomposition (as for the μ-peroxodecacyanide) not being possible because the μ-superoxodicobalt unit shows very low basicity (as evidenced by the lack of dependence of the spectra of the complexes on solution pH). We will further discuss this point in the section following this one.

We can now consider the various possible electronic transitions in the μ-superoxo complexes. An intraligand assignment has been suggested[129] for the 14.9 kK band of the decaammine, primarily because work on an optically active ethylenediamine analogue failed to show strong circular dichroism for this band (which is certainly an additional strong argument against it being a d-d transition). The $\pi^* \rightarrow \pi^*$ ($^2B_g \rightarrow {}^2A_g$) transition is LaPorte forbidden and is therefore expected to be rather weak. Furthermore, the spatial overlap of these orbitals is poor and the transition would be expected to be much, much weaker than the observed transition. The $\pi \rightarrow \pi^*$ ($^2B_g \rightarrow {}^2B_u, {}^2A_u$) transition is allowed but, for one thing, would be expected to be more intense than observed, and for another, would probably not be strongly

polarized. (In any case, if one of the two transitions were more intense than the other, it would be the $^2B_g \rightarrow {}^2B_u$ (π out-of-plane $\rightarrow$ π^* out-of-plane) transition, which would be z-polarized.) Additionally, and more importantly, we expect this transition to remain at roughly the same energy as in the free O_2^- ion ($\sim$ 42 kK).[15] We thus conclude that an intra-ligand assignment is improbable.

We will now consider LMCT transitions. The intense transition observed at 33.1 kK (ϵ = 20,160) for the decaammine has the high intensity of an allowed $\sigma \rightarrow$ M charge transfer transition, and we assign it as π^* in-plane (O_2^-) $\rightarrow$ dσ^*(Co(III)). The unsplit ligand field bands in the spectrum indicate a very small splitting of d_{z^2} and $d_{x^2-y^2}$, and we assume that transitions to both metal orbitals are underneath the observed band envelope, with the transition to d_{z^2} expected to be far more intense. (We would thus predict this band to be polarized along the O_2 axis. Unfortunately, the high intensity of the band has precluded a determination of its polarization in the crystal. The data of Yamada, et al.,[127] incidentally, show rather obvious light leakage effects in this wavelength region.)

The decacyanide shows two charge-transfer peaks, at 33.16 kK (ϵ = 16,750) and 37.59 kK (ϵ = 5440), at 77°K. We assign these as the two components of the π^* in-plane $\rightarrow$ dσ^* transition, to d_{z^2} and $d_{x^2-y^2}$, respectively. Both the intensity pattern and the magnitude of the splitting are consistent with this assignment. The lower energy band shows a large shift to higher energy and a small decrease in apparent intensity with decreasing temperature.

These effects are probably mainly due to the decrease in intensity of the ligand field band shouldered on this band to lower energy. The lowest energy charge transfer band does not show a shift to higher energy relative to the band in the decaammine, and we note, as for the peroxide complexes, that the transition to $d_{x^2-y^2}$ is a better indication of the increase in Δ in the cyanide complex. A smaller shift than for any of the complexes considered in chapter 2 is indicated. $Co(CN)_5Cl^{3-}$ showed only a 700 cm^{-1} shift of its $\sigma(Cl^-) \rightarrow d_{z^2}$ transition to higher energy from $Co(NH_3)_5Cl^{2+}$, so the disparity is not very large. A possible explanation is that μ-O_2^- in the cyano complex has a slightly smaller π^* splitting than in the ammine complex, that is, that it is a weaker σ-donor in the cyano complex. The very close correspondence of the lowest ligand field band in the decaammine to that of $Co(NH_3)_6^{3+}$ at least suggests the possibility of such an effect, the μ-O_2^- ligand in the decaammine conceivably having a ligand field strength equal to or greater than that of NH_3. (This is, however, not a positive argument, as only a very small shift is expected if the μ-O_2^- ligand does have a ligand field strength close to that of N-bonded thiocyanate, as seems true for the decacyanide.) Considering the magnitude of the effect, more definite conclusions do not seem at all warranted.

Other transitions having been eliminated, we must necessarily assign the mysterious 14.89 kK (ϵ = 928) band of the decaammine, and also the (presumably analogous, and similarly

unassigned) 20.59 kK (ϵ = 745) band of the decacyanide, to a transition involving the half-filled π^* out-of-plane (b_g) orbital, either MLCT or LMCT. The LMCT transition, π^* out-of-plane → $d\sigma^*$, is rather analogous to a π(halide) → $d\sigma^*$ transition, and the observed intensities might therefore be reasonable for such an assignment. The spectroscopic π^* splitting of 18.5 kK implied for the decaammine by the assignment seems extraordinarily large in comparison to the σ-π charge transfer splittings of 7-8 kK observed for halide complexes in chapter 2, but various electron repulsion parameters, whose magnitude is difficult to predict, enter into the transition energies and make such comparisons fallible. (Hexahalometalate complexes show σ-π charge transfer splittings of ~ 12-15 kK,[48] while the diatomic hydrogen halides show vertical ionization energies indicating σ-π separations of ~ 30 kK.[130] It seems likely that electron repulsion effects considerably reduce the splittings of the charge transfer states of halide complexes from the one-electron energy separation of the π and σ levels.)

However, we would, again by analogy to halide charge transfer, expect the component of this transition to d_{z^2} to be more intense than that to $d_{x^2-y^2}$, and thus predict the transition to be z polarized, whereas, as noted earlier, the transition in the decaammine is strongly polarized along the O–O direction. Exhibition by a transition to $d_{x^2-y^2}$ of intensity comparable to that shown by the transition to d_{z^2} could perhaps be tolerated, but for

the transition to d_{z^2} to show much less intensity would seem somewhat freakish. An additional argument against this assignment is that the band in the decacyanide shows a large blue shift (somewhat in contrast to the higher energy LMCT transition) without apparent large splitting. This behavior seems more consistent with an assignment involving the metal $d\pi$ orbitals.

An MLCT assignment is such an assignment. The specific transition we expect to observe in superoxide complexes is $d\pi \rightarrow \pi^*$ out-of-plane. (This transition is, of course, not possible in peroxide complexes, and a low energy transition is not observed, which was an early reason for our favoring such an assignment.) There are three possible $d\pi \rightarrow \pi^*$ transitions, but one of these, involving the $d\pi$ orbital which can be involved in π-bonding (b_g, in C_{2h}), is expected to be more intense than the others, and the predicted polarization is therefore, gratifyingly, along the O-O direction.

MLCT transitions are usually of quite high energy for d^6 complexes (the metal-to-cyanide charge transfer discussed in chapter 2 being the best established example of such a transition), which is clearly related to the high ionization potential of Co(III). However, the present case of a half-filled ligand orbital is obviously a rather special one. One can argue that, for these complexes, it would be surprising if an MLCT transition were <u>not</u> observed, and failing to assign the observed "anomalous" band as an MLCT transition would produce an unsettling lack of another band to assign.

The band is strongly blue-shifted in the decacyanide, by 5.7 kK. Comparative examples are very scarce, the only possible such being the nitro complex discussed in chapter 2, which similarly showed a very large shift of a band assigned as MLCT (4.5 kK), especially in comparison to the small shift observed for the observed LMCT transition (to d_{z^2}), which again is analogous to the present case. We discussed possible reasons for the observed shifts, and that discussion also applies to the μ-superoxo complexes.

Not enough μ-superoxo complexes with other ligands are known to allow very comprehensive correlations of the energy of the MLCT band with ligand field strength. Analogous dimers are known with a variety of multidentate amine ligands, and these show a band at 700-710 nm,[113] slightly red-shifted relative to the decaammine. This is the opposite of the trend expected for an LMCT transition, as these amines generally show a slightly stronger ligand field than NH_3. (On the other hand, it is not at all clear how a MLCT transition should shift.) Similarly, the L-histidinate complex,[131] which has CoN_4O_2 chromophores, has a band at 680 nm, negligibly shifted. (Although the ligand field bands of the above mentioned complexes are somewhat scattered and not easily analyzable, it is striking that, where both the μ-peroxo and μ-superoxo complexes are known, the μ-peroxo complex consistently shows a lower-energy ligand field band, by 2-3 kK, consistent with our previous analysis of the ligand field strengths of the two ligands.)

One particularly striking comparison does exist, however, A number of complexes $XRh(py)_4-O_2-Rh(py)_4X^{3+}$ have been reported,[132] and these show a band at ~17 kK, with an ϵ of ~3000. It seems quite inconceivable that the band could be LMCT and appear at such low energies in a Rh(III) complex. (The band also shows a dependence on the trans ligand, moving from 16.6 kK for $X = Cl^-$ to 17.5 kK for the aquo complex, casting doubt on an intraligand assignment, above and beyond our previous arguments in that regard. Further, some μ-peroxo complexes are reported, and do not show the low-energy band.) For a MLCT assignment, on the other hand, while a blue-shift going from Co(III) to Rh(III) is probably expected, nothing in our expectations prejudices us against such a relatively small shift. (Actually, the Co(III) analogue is unknown, as is, correspondingly, the magnitude of the shift, but it is probably not very unreasonable to make comparisons to the decaammine.) Iridium(III) pyridine complexes, for example, are reported to show $d\pi \rightarrow \pi^*$(pyridine) MLCT transitions at 30-35 kK,[133] showing rather small blue, and perhaps even red shifts from the first and second row.

The MLCT bands show rather unusual temperature behavior. For both the decaammine and the decacyanide, the bands show an apparent increase in integrated intensity at 77°K. The maximum of the decaammine does not show a very large shift with temperature, but the band becomes distinctly asymmetric. This could possibly be due to resolution into two or more components separated

by 1000 cm^{-1} or so (transitions from the various $d\pi$ orbitals) but could also be due to incipient resolution of vibrational structure, which is suggested by the shape of the band. Also at 77 °K, a weak shoulder is discernible on the low energy side of the band, for which we will momentarily consider assignments.

The decacyanide band does not give evidence of resolving into component transitions at 77 °K, and, in fact, very noticably broadens, to lower energy, an entirely out-of-the-ordinary effect. The explanation of this effect is very possibly connected to the intriguing dependence of the maximum of the band at room temperature on environment.

While the crystalline decacyanide is magenta, dilute solutions are orange. Potassium bromide pellets of the decacyanide have (visually) the same color as the crystalline salt and, as shown in figure IV-9, the maximum of the MLCT band in KBr pellets is observed to be at 523 nm (19.15 kK), a shift to lower energy of nearly 1500 cm^{-1} from the solution maximum. The decaammine, on the other hand, shows no such effect, the maximum in KBr pellets being essentially identical to the solution maximum. It seems natural to ascribe this difference in behavior to the obvious fact that the decaammine is a highly charged cation while the decacyanide is a highly charged anion. We early observed that concentrated solutions of the decacyanide are red, and the same effect can be induced simply by increasing the concentration of potassium ion, 0.2 M KCl, for example, shifting

the observed maximum from 485 nm to 490 nm. (The lithium ion does not cause a large effect, at least at room temperature, aqueous solutions either with or without high concentrations of LiCl having essentially the same spectrum.) The inferred interaction of the potassium cations with the decacyanide anion is probably above and below the Co-O_2-Co plane with the high-energy π^* out-of-plane orbital (with such an interaction being prohibited for the decaammine cation by its high charge). Such (loosely speaking) "solvation" interactions could lower the energy of an electronic transition either by increasing the energy of the ground state or by decreasing the energy of the excited state (in the ground state configuration). The first possibility seems rather unlikely, but the second is highly consistent with the assignment of the band. The MLCT transition should increase the population of the π^* out-of-plane orbital (giving, formally, peroxide), and a positively charged environment should therefore be energetically favorable. (The high energy LMCT band shifts to high energy in the solid and at low temperature. While other explanations can account for part or all of this shift, we note that the direction of the shift is consistent with the assignment, by arguments similar to those presented above.)

A possible explanation for the 77 °K spectral results, then, is that at low temperatures the anions "freeze out" with closely associated alkali metal cations. The band does not shift as strongly to lower energy as it does in the solid, which is consistent

with less complete ion-pairing than in the solid potassium salt.

We have not yet considered the question of where the expected π^* out-of-plane → d_{z^2} LMCT transition is. For μ-peroxo complexes we observed transitions from both π^* orbitals, and the geometry of the μ-superoxo complexes is a limiting case of the μ-peroxo geometry, for a torsional angle of 180°. It seems likely, from the π^* splittings observed for the μ-peroxo complexes, that the π^* out-of-plane → d_{z^2} transitions in the decaammine could occur as low as 550 nm. Inspection of the decaammine spectrum in this region shows that a weak transition could avoid observation here. For the decacyanide, a similar transition energy would be expected, assuming a roughly constant π^* splitting, and here the MLCT transition might obscure the transition. This explanation grades imperceptibly into a second possible explanation, which is that the transition is simply too weak to be observed.

Finally, we will consider the possible energies of the two predicted intraligand transitions. For both the decaammine and the decacyanide, we observe shoulders at 44-45 kK, with ϵ's of ~20,000 for the decaammine and ~14,000 for the decacyanide, the transition being better resolved for the decacyanide. The close correspondence to the $\pi \rightarrow \pi^*$ transition of free O_2^- ion at 42 kK[15] suggests that this may be the $\pi \rightarrow \pi^*$ transition of the complexed ligand, the energy of this transition not being expected to change greatly, as noted earlier.

We have previously noted that we observe a weak shoulder in the decaammine spectrum at 12.7 kK ($\epsilon \simeq 130$), which is fairly well resolved at 77°K. This band is at about the same energy as the lowest energy singlet-triplet ligand field transition in $Co(NH_3)_6^{3+}$,[99] but the intensity seems exorbitantly high for an analogous assignment, even with a nearby charge-transfer transition from which to "steal" intensity. In the spectrum of the decacyanide we observe a weak but very well resolved transition at 12.3 kK, $\epsilon = 14$, as shown in figure IV-10. Photolysis of the decacyanide at 313 nm causes the 20.6 kK and 12.3 kK bands to disappear at the same rate, hence we infer that, despite its weakness, this band is an authentic band of the decacyanide ion. The energy of this band is far too low for it to be a singlet-to-triplet ligand field band in the decacyanide, and we suggest that it is the $^2B_g \rightarrow {}^2A_g$ ($\pi^* \rightarrow \pi^*$) transition, expected to be weak as previously discussed. The close correspondence in energy to the shoulder in the decaammine suggests a similar assignment. The energy of this transition should be a relatively direct measure of the one-electron splitting of the π^* level (with the usual vitiating details of unknown electron repulsion parameters) and the inferred bonding energetics seem qualitatively reasonable.

At this point, we can briefly summarize the properties found for μ-O_2^- ligands in Co(III) complexes. The ligand field strength of O_2^- is comparable to and probably slightly higher than that of N-bonded thiocyanate, and greater than that of O_2^{2-}. (A

reasonable rationale for the increased ligand field strength is that π-donor capability is reduced in O_2^-, with σ-bonding probably remaining of similar magnitude.) Ligand-to-metal charge transfer is observed at very similar energy to that observed for the peroxide complexes, with transitions being observed only from one π^* level, presumably the π^* in-plane bonding level. Low energy metal-to-ligand charge transfer is observed to the half-filled π^* out-of-plane level. Finally, we observe transitions which we tentatively assign to the intraligand $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$ transitions, the energy of the former implying a π - π^* out-of-plane splitting not very different from that in the free O_2^- ion, and the energy of the latter indicating a π^* splitting of a magnitude implying that $\pi^* \rightarrow d\sigma$ bonding interactions can account for the metal ion-superoxide chemical bond.

Somewhat in the fashion of an afterthought, we can now consider Co(III) superoxide monomers. In addition to transient intermediates, stable monomers are known with a variety of (primarily) nitrogen donor ligands having π-systems, including porphyrins,[134] corrins,[135] glyoximes,[136] and Schiff bases.[137, 138, 139] Eight-line esr spectra characterize the complexes as monomers in solution, with further analysis[139] indicating the complexes to have "end-on" bound superoxide groups, the unpaired electron being heavily localized on the oxygens. Further, some monomers with Schiff base ligands have been crystallized, the published crystal structure[140] of

Co(bzacen)(py)(O_2) (where bzacen is N,N′-ethylenebis(benzoylacetoniminide) showing the Co-O-O angle to be 126°.

For all of these complexes, electronic spectroscopy is of extremely limited value, as spectra are generally dominated by transitions involving the equatorial ligands, either intra-ligand or charge-transfer. For porphyrins and similar ligands, the problem is quite impossible because of very intense ligand transitions. Schiff base spectra are somewhat similar, and the oxygen adducts of Co(II) Schiff base complexes are generally observed to be highly colored,[137,138] rather more so than "normal" Co(III) Schiff base complexes. For the oxygen adduct of Co(salen), where salen is N,N′-ethylenebis(salicylaldehydeiminate) (as well as for substituted derivatives) we observe shoulders at 700 to 725 nm. (KBr pellet spectra of the oxygenated "active" form[137]) which might correspond to the expected low-lying MLCT π^* out-of-plane → $d\sigma^*$ transition. This transition has also been noted in solution.[141] The energy of the π^* out-of-plane orbital should not be very different in the monomer and dimer, and the ligand field strengths of the Schiff base ligands are close to that of NH_3, so the energy of the transition would seem reasonable.

However, the aforementioned low energy ligand transitions make the assignment somewhat speculative. (That the band is observed as a shoulder is particularly indicative of this.) It would be "nice" if monomers without such ligands could be investigated

but it seems likely that the high energy π and π^* levels of these ligands are essential in stabilizing the monomers.

The stability of a monomer relative to a dimer is a function both of the strength of the primary interaction of O_2 with the Co(II) complex (the reversibility of the reaction for these complexes indicating a relatively close comparison to $Co(NH_3)_5^{2+}$), and of the "nucleophilicity" of the uncomplexed end of the O_2 unit in the monomer. The clearly much greater tendency toward dimer formation in the NH_3 system indicates that the π donor, acceptor character of the nitrogen ligands is probably a major factor. More precisely, it seems likely that π acceptor interactions are very important.

Co(salen) can be reduced to $Co(salen)^-$ and $Co(salen^{2-}$,[143] with the complexes probably being best formulated as a Co(I) complex, and a Co(I) complex of a reduced ligand, respectively. The Ni(II) and Cu(II) complexes are also reducible, in which cases the reduction very probably takes place solely on the ligand. These results indicate that the complexed ligand has very low-lying empty π orbitals, which should clearly be capable of π-acceptor interactions with the central metal ions.

Crudely, such interactions are expected to increase (at least, potentially) π-donor interactions of O_2^- and O_2^{2-} ligands with the central metal ion, and, again, crudely, this should lead to an increase in complexed O_2 bond strength and a decrease in the negative charge of the uncomplexed oxygen of monomers, due to the

formal decrease in π^* occupation. It thus seems possible that the conjugated nitrogen ligands stabilize monomers by acting as π-electron sinks, and producing dioxygen ligands which are formally closer to neutral dioxygen. (Looking at the complexes from the alternative viewpoint of a dioxygen molecule forming a bond with a Co(II) complex, we would say that the O_2 unit oxidatively removes an electron from the cobalt d_{z^2} $d\sigma^*$ orbital, but ends up partially giving it back up to the cobalt $d\pi$ orbitals, which are "depleted" by donation to nitrogen ligand π^* orbitals.) The magnitude of interaction necessary to produce such effects is not necessarily in conflict with our earlier characteristic of the upper π^* level in superoxide complexes as a primarily non-bonding level.

Many of the Schiff base adducts do crystallize as dimers, and a reported crystal structure[142] shows, interestingly, a structure similar to that of the previously discussed μ-peroxo complexes, except that the O-O bond length is only 1.35Å, 0.12Å less than that in the μ-peroxo decaammine. Such an effect can be discussed in terms of a hybrid of valence bond structures, but we note in passing that it is also consistent with the analysis above. As π-donor interactions are probably fairly important in the bonding description of the μ-peroxo decaammine, some rather drastic effects might have been expected for a Schiff base dimer.

A final possible example of a superoxide monomer is $Co(CN)_5O_2^{3-}$, which reportedly[144] crystallizes as a monomer,

with tetralkylammonium cations, from acetonitrile solution. The primary support for the monomeric formulation is the observation of an eight-line esr spectrum for a solution of the complex in acetone (the solid or acetonitrile solutions giving unresolved signals). The explanation given for the reaction stopping at a monomer in non-aqueous solution is that the bulky tetraalkylammonium cations prevent close approach of two anions, which actually seems rather reasonable.

However, the reported electronic spectrum is strikingly similar to that of the μ-peroxo decacyanide ion discussed earlier, showing a peak at 322 nm ($\epsilon \simeq 4400$) and a shoulder at ~ 400 nm ($\epsilon \simeq 2000$). The wavelengths and the intensities/cobalt are comparable to those of the dimer. Unfortunately, the reported spectrum does not extend beyond 450 nm, preventing further analysis.

We frankly do not understand this correspondence if both the dimer and monomer are correctly formulated. We have already mentioned that the dimer is not really well characterized, and it is conceivable that the "dimer" has nonequivalent cobalt atoms, and is not a true dimer. It is rather difficult to conceive of an alternative structure, however. Alternatively, the reported monomer might really be a dimer, with the esr signal arising from some impurity level of monomer, or perhaps even from monomer generated from μ-superoxo dimer upon solution in acetone, the μ-superoxo dimer being a probable impurity in any preparation of

μ-peroxodimer. (We note that elemental analysis cannot adequately distinguish between a monomer and a dimer.) We have no proof of any kind for any of the above suppositions, and remain neutral but suspicious.

Thermal and Photochemical Reactions of μ-Superoxo Dimers

The chemical reactions of μ-superoxo dicobalt complexes can be divided into redox reactions, which are dominated by reaction at the superoxide ligand,[119] and substitutional reactions, which seem to be qualitatively well described as those of Co(III) complexes.

The μ-superoxo decaammine complex is only stable in acidic solution, which seems to be related to an extremely rapid base hydrolysis reaction. In acidic solution, thermal decomposition may be interpreted[145] in terms of the mechanism

1) $$(NH_3)_5CoO_2Co(NH_3)_5^{5+} + H_2O \longrightarrow Co(NH_3)_5(OH_2)^{3+} + Co(NH_3)_5O_2^{2+}$$

2) $$Co(NH_3)_5O_2^{2+} \xrightarrow{\text{fast}} Co^{2+} + 5NH_3 + O_2$$

The rate shows no dependence on $[H^+]$. At 65 °C the rate parameters $k = 6.7 \times 10^{-5}$ sec^{-1}, $\Delta H^{\ddagger} = 28.1$ kcal-mol^{-1}, and $\Delta S^{\ddagger} = 17$ eu are obtained.[145] Only the entropy term, which is slightly higher than those generally observed, is exceptional in any way for a $Co(NH_3)_5X^{2+}$ aquation reaction.

The photochemical decomposition of the complex has been interpreted in terms of a similar reaction scheme,[146,147]

3) $(NH_3)_5CoO_2Co(NH_3)_5^{5+} \xrightarrow{h\nu} [(NH_3)_5CoO_2Co(NH_3)_5^{5+}]^*$

4) $[(NH_3)_5CoO_2Co(NH_3)_5^{5+}]^* \longrightarrow Co(NH_3)_5O_2^{2+} + Co(NH_3)_5^{3+}$

5) $Co(NH_3)_5^{3+} + OH_2 \xrightarrow{\text{fast}} Co(NH_3)_5OH_2^{3+}$

or

6) $[(NH_3)_5CoO_2Co(NH_3)_5^{5+}]^* \longrightarrow Co(NH_3)_5O_2^{3+} + Co(NH_3)_5^{2+}$

7) $Co(NH_3)_5O_2^{3+} \xrightarrow{\text{fast}} Co(NH_3)_5^{3+} + O_2$, etc.

with the photoredox reactions usually observed in cobaltammine photochemistry complicating interpretation. The low energy bands at 14.9 kK and 20.8 kK are not observed to have photochemistry associated with them, while the disappearance quantum yield approaches 0.3 at higher photon energies.[147] A $Co(NH_3)_5^{3+}$ intermediate which can be trapped in the presence of complexing anions is definitely produced.[147] Photolysis with 254 nm light is reported[146] to give (with a net reduction in quantum yield over 313 nm irradiation) free radical products probably associated with O-O bond scission, which is interesting in view of our assignment of a $\pi \rightarrow \pi^*$ transition at a nearby energy. Such a transition should formally give an O-O bond order of only one half, presenting the possibility of such reactions, and the excited state might be expected to show poor internal conversion to other excited states of the complex, accounting for the decrease in quantum yield.

Data are somewhat more lacking for the decacyanide, and we have investigated the thermal and photochemical aquation

reactions of this ion. Disappearance rates are quite simple to obtain because of the low energy (20.6 kK) absorption peak, none of the products having absorption in this region.

In table IV-3, we show kinetic data we have obtained for the thermal decomposition of the decacyanide in aqueous solution (without added electrolytes). The eventual products of the reaction are $Co(CN)_5OH_2^{2-}$ and (presumably) H_2O_2, but at intermediate points in the reaction enhanced absorption in the vicinity of 300 nm is noted, which we tentatively ascribe to peroxide complexes. The reaction is quite insensitive to pH.

A reasonable first step in the mechanism is

8) $$(CN)_5CoO_2Co(CN)_5^{5-} + H_2O \rightarrow Co(CN)_5OH_2^{2-} + Co(CN)_5O_2^{3-}$$

and we infer that the superoxide monomer thus formed does <u>not</u> dissociate to O_2 plus $Co(CN)_5^{3-}$, as in our reaction medium pentacyanocobaltate(II) would relatively rapidly dissociate to give Co(II) (aq). The actual mode of decomposition of the monomer in the absence of any reducing agents is rather unclear, with a "disproportionation" reaction

9) $$2\,(CN)_5CoO_2^{3-} \rightarrow (CN)_5CoO_2Co(CN)_5^{6-} + O_2$$

being a likely but completely unproved possibility.

We find a good straight line fit for a log k versus 1/T plot, and evaluate the activation parameters $\Delta H^{\ddagger} = 24.0$ kcal mole^{-1} and $\Delta S^{\ddagger} = -5.7$ eu. For comparison, aquation of $Co(CN)_5N_3^{3-}$

Table IV-3

Kinetic Data for the Decomposition of $[(CN)_5CoO_2Co(CN)_5]^{5-}$ [a]

k (sec^{-1})	temperature, °C	
1.16×10^{-5}	51.5	
1.25×10^{-4}	74.0	$\Delta H^{\ddagger}$ = 24.0 kcal/mole
3.84×10^{-4}	84.3	$\Delta S^{\ddagger}$ = -5.7 e.u.
4.36×10^{-4}	75.8[b]	

[a] Monitored by following decrease in absorbance at 485 nm. In aqueous solution with no added electrolytes unless otherwise noted.

[b] 0.05 M phosphate buffer, pH 7.

is characterized by the values[148] $\Delta H^{\ddagger} = 27.3$ kcal mole^{-1} and $\Delta S^{\ddagger} = -0.6$ eu. The value of $\Delta H^{\ddagger}$ seems very reasonable and consistent with expectations. The value of $\Delta S^{\ddagger}$ evaluated is rather surprisingly negative, however, for which we have no ready explanation. (Ion-pairing effects are conceivably involved.) Part of the discrepancy in comparison to the reference values possibly is due to their having been determined in unit ionic strength medium. The last entry in table IV-1 indicates about a 20% increase in rate in a higher ionic strength medium.

In table IV-4 we show disappearance quantum yields for the decacyanide. The product of the reaction is, again $Co(CN)_5OH_2^{2-}$, and a mechanism producing $Co(CN)_5^{2-}$ and $Co(CN)_5O_2^{3-}$ is probably indicated. Comparison with the values for sulfite complexes presented in chapter 2 shows that the complex is extremely photochemically reactive, having a very much larger accentuation of excited state reactivity over ground state reactivity than most pentacyanocobaltate complexes.

We find, in agreement with Valentine and Valentine,[147] that irradiation into the 20.6 kK (48.5 nm) band gives very much smaller photochemical reactivity. Furthermore, we have irradiated into the very weak 812 nm band (with a filtered projector lamp) and find no photochemical reactivity here.

The "abnormally" high quantum yield for 366 nm irradiation can perhaps be justified in terms of the electronic structure of the ion. We previously mentioned that the bonding for a bridging

Table IV-4

Disappearance Quantum Yields for $[(CN)_5CoO_2Co(CN)_5]^{5-}$ [a]

Irradiation Wavelength	Quantum Yield (± estimated uncertainty)
366 nm	0.47 ± 0.05
313 nm	0.70 ± 0.05
254 nm	0.50 ± 0.10

[a] Measured by following decrease in absorbance at 485 nm. In 0.05 M phosphate buffer, pH 7.

superoxide ion must necessarily be rather special. Conceivably, upon an excitation such as a ligand field transition, which removes the indistinguishability of the cobalt centers (and reduces the σ bonding in the excited center), the electronic structure of the bridging O_2^- ligand might readjust so as to concentrate bonding on the other center (as in HO_2), leaving the excited center extremely labile. This explanation could still hold if the reaction came from a lower state (such as a hot ground state) since the excess energy would still be expected to be initially concentrated on one of the cobalt centers.

In distinct contrast to sulfito complexes, a large (outside of experimental error) increase in quantum yield is observed for 313 nm irradiation. An increased quantum yield at a higher energy has many possible explanations, one of the simplest being that the nearby LMCT state shows direct photochemical reactivity. The reactivity could be described by an argument similar to the one used for 366 nm irradiation.

Irradiation at 254 nm appears to give reduced quantum yields, close to the 366 nm values. As the 254 nm value is much less accurate than the others, we will not attempt to discuss it. For short irradiation times at 254 nm we observed very high quantum yields between 2 and 3, the reaction rate rapidly settling down to give the value reported in table IV-4 over longer irradiation times. We tentatively ascribe this biphasic behavior to free radical reactions catalyzed by impurities present in low

concentrations in the solutions, depletion of the impurities at long irradiation times leading to the less efficient photochemical reaction represented by the listed quantum yield.

We have also searched for cyanide aquation (disubstitution) products, by the sulfite method described in chapter 2. Although the very high quantum yields of the major process do not allow much accuracy in the determination of the quantum yield of a minor (inefficient) reaction, we do detect real production of disubstituted products in the photoreactions, quantum yields at 254 nm and 313 nm being of the order of 0.02. No disubstituted products were formed in thermal aquation. By the correlations of chapter 2, this could be interpreted to mean that O_2^- is a π-donor.

We recognize two mechanisms for wavelength effects on quantum yields. First, that different excited states may show different direct photochemical reactivities, or may populate a reactive excited state (by intersystem crossing) with different efficiencies. Second, that different excited states may cross to a reactive state (which might be the ground state) which has more or less vibrational excitation (hence reactivity) depending on the state from which it was entered. (A possibility also exists for a dependence on the vibrational excitation of the initial excited state but this seems unlikely as we naively expect vibrational relaxation to be much faster than intersystem crossing. It is, however, clearly possible that intersystem crossing might be most efficient

for an excited vibrational level of the excited state, which could be of consequence.) The second mechanism implies a primarily monotonically increasing quantum yield with decreasing wavelength, but decreases can easily be reconciled if we recognize that vibrational excitation in the reactive state could show up in different vibrational modes as a function of the initial state, some of which could lead to reaction more directly than others.

Electronic absorption in acidopentacyanocobaltate complexes is distinctly banded, which strongly implies that the excited states are not dissociative and that chemical reaction occurs from some other state(s), triplet states, hot ground states, or perhaps "non-spectroscopic" states involving geometric distortion. The experimental evidence at hand is quite insufficient to distinguish the various possibilities, however. In chapter 2, we noted a decrease in quantum yield at 313 nm which we ascribed to population of a $^1A_2$ ligand field state. This is reasonable either on the grounds of the bonding in this state, or on the grounds of the vibrational modes expected to be excited on intersystem crossing from this state, the $^1E^a$ ligand field state being expected to yield vibrational excitation primarily of the (presumably reactive) Co-X stretching mode. The reaction might proceed either from a triplet state or from the ground state, but in the later case we would probably have to assume that the molecules in the different excited states did not pass through some common state (such as a triplet) on the way to the ground state.

It seems much simpler to assume that a reactive excited state is responsible for the wavelength effects. The results for the decacyanide lend some (but hardly conclusive) support to this hypothesis. That the MLCT state responsible for the 485 nm band is unreactive is not very surprising--chemical bonding of the O_2 unit and the cobalts in this excited state would probably be stronger than in the ground state. However, the lack of reactivity also implies that the hot ground state obtained by crossing is also unreactive. The energy of the excited state is very much greater than the activation energy for thermal dissociation, and vibrational energy in the ground state would be initially concentrated in modes of the CoO_2Co unit. If a hot ground state is responsible for the reaction resulting from the higher excited states, it is thus not at all clear why reaction does not result here. A simple solution is that the reactive state (or states) is some state which is at higher energy than the MLCT state, or for which internal conversion from the MLCT state is very inefficient.

We would like to be able to discuss the increase in quantum yield noted near the LMCT state in more detail, but do not feel that this is called for because the number of available states (both spectroscopic and non-spectroscopic) at high energy is so much greater than in simple acidopentacyanocobaltates.

Finally, we feel obliged to note that our quantum yields are very much greater than those reported by Valentine and

Valentine.[147] The major reason for the discrepancy is the very low value for the molar extinction coefficient of the decacyanide used by Valentine and Valentine, and we assume that their compound was markedly impure.

"End-On" Peroxide and Superoxide Complexes of Other Metal Ions

Peroxide complexes have been reported for nearly every transition metal.[149] Many of these have the symmetrical structure to be discussed in the chapter following this one, and most are extremely poorly characterized. In closing out this chapter, we are going to consider a limited number of complexes which at least probably have the "end-on" structure and which we consider to be particularly interesting.

We have already mentioned the μ-peroxo and μ-superoxo complexes of rhodium(III) with pyridine ligands.[132] A rhodium(III) complex which can probably be reformulated as $Rh(CN)_5(O_2H)^{3-}$ in view of recent work on the precursor, $Rh(CN)_5H^{3-}$,[124] has also been reported.[104] This complex predictably shows all bands strongly shifted to higher energy. The only reported maximum at 238 nm (ϵ = 210) is presumably the $^1A_1 \rightarrow {}^1E^a$ ligand field transition. The energy of this transition is surprisingly high, compared with 265 nm for $Rh(CN)_5OH_2^{2-}$ and 225 nm for $Rh(CN)_6^{3-}$.[47] At any rate, the spectrum of this complex lends support to the assignment of the bands in the spectrum of $Co(CN)_5(O_2H)^{3-}$ as ligand field and charge transfer transitions, rather than intra-ligand transitions.

Adams, et al.[150] have reported the isolation in solution of a μ-peroxo chromium(III) complex, $(H_2O)_5CrO_2Cr(OH_2)_5^{4+}$, by ion exchange chromatography of the products of H_2O_2 reduction of acidic CrO_3 solutions at low temperature. A trimer, $(H_2O)_5CrO_2Cr(H_2O)_4O_2Cr(H_2O)_5^{5+}$, can also be separated. These complexes, although they have not been isolated as solids, have been very adequately analytically characterized. (The activation parameters for aquation of the dimer, $\Delta H^{\ddagger} = 21.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.3$ eu, show the complex to be a normal Cr(III) complex. Compare $\Delta H^{\ddagger} = 23.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.5$ eu for $Cr(OH_2)_5Br^{2+}$.[151] The trimer shows very similar activation parameters.) The probable reason for the absence of such complexes in the products of oxygenation of Cr(II) solutions is the reduction of μ-peroxo dimers by Cr(II) to dihydroxy-bridged dimers.

The electronic spectra of the complexes show two intense bands at ~ 270 nm and ~ 230 nm (a separation of ~ 6 kK), which are probably assignable to ligand-to-metal charge transfer transitions from the split O_2^{2-} π^* level. $Cr(OH_2)_5I^{2+}$ shows a σ charge transfer band at 260 nm ($\epsilon = 5740$),[152] indicating the energy of the observed transitions to be reasonable.

In the visible, two bands are observed for the dimer at 634 nm and 439 nm, with absorption coefficients per chromium of 202 and 153. These bands are at almost the same energy as the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ (^4F) ligand field transitions of

$Cr(OH_2)_6^{3+}$, but have ϵ's higher by a factor of 10 to 20. The trimer shows bands at very similar energies, with the intensity per chromium double that of the dimer. No such huge intensity effects are observed in the spectra of other monosubstituted chromium(III) species, $Cr(OH_2)_5I^{2+}$ showing only a factor of 3 intensification over the hexaaquo complex.[152]

Comparable intensification effects are observed in the μ-oxo complex $(NH_3)_5CrOCr(NH_3)_5^{4+}$,[153] and are here attributable to strong coupling of the two d^3 metal centers, evident in the antiferromagnetic temperature dependent magnetic behavior. (Such coupling is not possible for cobalt(III) complexes, which have full $d\pi$ shells.)

The spectrum of the μ-oxo complex also has sharp, moderately intense ($\epsilon \simeq 1000$) bands between 300 and 400 nm, assigned as spin-doublet "simultaneous excitations" (coupled with Cr → Cr charge transfer transitions.)[154] The spectra of the μ-peroxy complexes do not give any evidence of such transitions. A simple conclusion would be that the Cr(III) centers in these complexes are indeed coupled by π interactions through the μ-O_2^{2-} group, but not as strongly as in the μ-O^{2-} complex. Considering the level of our understanding of such systems, however, further proof seems called for. Actually, the bands observed for the μ-O_2^{2-} complexes are surprisingly sharp, and it is tempting to ask whether these might not be anomalously intense quartet-doublet transitions (expected at similar energies) superimposed on the

quartet-quartet transitions. (The observed bands are noticably asymmetric to higher energy.) This suggestion is best described as a flight of fancy, of course. The question of the suitability of O_2 units as transmitters of "magnetic" interaction remains substantially unanswered and is deserving of further investigation.

Ferric EDTA forms a strongly colored violet complex with hydrogen peroxide at pH's greater than 8.[106] The source of the color is a band at 515 nm, $\epsilon \simeq 510$. Our attempts to isolate this complex have uniformly failed. Iron complexes often catalyze the disproportionation of peroxide and Fe(III)EDTA seems to be no exception in concentrated solution. Nonaqueous solvents also seem to induce decomposition. Studies of the complex have therefore been restricted to solution work.

The complex is assuredly a monomer, as shown by the concentration dependence of the absorbance. The composition of the complex is somewhat less certain, as fitting to the known solution equilibria of ferric EDTA and H_2O_2 has not been entirely successful. A stoichiometry of one peroxide per iron is certain, but whether or not a hydroxide is also coordinated to the Fe(III) is unclear. Formulation of the complex as an unprotonated peroxide complex is suggested by the report of George et al.[154] that hydroperoxyferric complexes have little absorbance in the visible. However, comparison to the charge transfer band of $Fe(OH_2)_5NCS^{2+}$ at 480 nm[155] and to $Co(CN)_5O_2H^{3-}$ would seem to favor a hydroperoxide complex, as would also the observation of only a single

band (rather than two highly split bands corresponding to bonding and non-bonding π^* levels.) The spectrum of the EDTA peroxide complex relative to George's hydroperoxide complexes could be explained if the band in the EDTA complex were from the non-bonding π^* level of an $Fe\text{-}O_2^+$ unit, the transition from the bonding level then presumably being in the ultraviolet. The comparison to the isothiocyanate complex, however, makes this seem rather unlikely. It does not at all seem likely on many grounds that a true Fe(III) hydroperoxide complex would show only high-energy charge transfer. A variety of other amino acid ligands form ferric peroxide complexes at high pH's. None of these show any advantage in stability, and most show lower stability.

Finally, we will discuss a system which we consider primarily because we invested considerable effort in attempting to improve the characterization of the complex (without very much success).

Ezerskaya and Solovykh[107] have reported that basic solutions of Ru(III)EDTA react slowly with dioxygen to give a green complex formulated as a dimer and containing one equivalent each of hydroxide and peroxide per formula unit. A non-crystalline solid was isolated which analyzed as $KNa_2[(EDTA)Ru\text{-}\mu\text{-}(O_2, OH)\text{-}Ru(EDTA)] \cdot 4H_2O$, presumably containing Ru(IV). The compound is diamagnetic. A complex having very similar spectral properties is reported to be formed rapidly in acidic solution by addition of hydrogen peroxide to Ru(III)EDTA solution[156] (having a relatively

short lifetime at these pH's because of catalyzed disproportionation of H_2O_2). This is rather more suggestive of a Ru(III) formulation, but hardly conclusive. Products were isolated containing varying amounts of halide ions, etc. and a dimeric formulation with Ru(IV) again suggested.

We were interested in this complex because of its possible relationship to the active site of the oxygen-carrying metalloprotein hemerythrin (to be discussed in another chapter) and therefore reinvestigated it.

The electronic spectrum of the complex shows a band at 632 nm ($\epsilon \simeq 125$), responsible for the green color of the complex, and an intense band at 392 nm ($\epsilon = 7700$). The intensities of shoulders observed at ~ 305 nm and ~ 440 nm are very much a function of sample preparation and must correspond to decomposition products. The band at 632 nm has a counterpart in the spectrum of the brown complex of Ru(III)EDTA in base, at 555 nm ($\epsilon = 140$), but not in monomeric complexes, and is presumably related to the dimeric nature of the complex. The band at 392 nm is presumably a peroxide charge transfer band. The noticeable lack of reliable spectral work on ruthenium complexes, as well as the decidedly uncertain nature of the complex, does not allow us to confidently assign the spectrum.

We were primarily interested in crystallizing the complex so as to be able to do a crystal structure and have some basis for further discussion. As described in the experimental section, we were completely unsuccessful.

The complex remains interesting, especially as a possible d^5 peroxide complex, and also from the viewpoint of magnetic interactions. All of this information remains well hidden, however.

A possibly related system is the manganese(II) salen system, for which a complex formulated as $[Mn(salen)_2]_2O_2$ has been reported.[157] A magnetic moment of 2.79 B.M. was reported, indicating a fairly strong magnetic coupling. We briefly investigated this system, and found that a rather bewilderingly large number of different compounds, many crystalline, were obtainable from various solvents and reaction conditions, most of which probably had oxo ligands. Electronic spectroscopy is, as for the coablt complexes, of little use. Crystal structure determinations are undoubtedly called for.

CHAPTER V

Complexes of Symmetrically Bound Dioxygen

Introduction

In 1963, Vaska[158] reported that the iridium(I) complex trans-$Ir(PPh_3)_2(CO)Cl$ reacted reversibly with dioxygen to give a 1:1 complex. The crystal structure, published soon afterwards,[159] showed the dioxygen unit to be symmetrically bound to the metal, the MO_2 unit forming an isosceles triangle, with an O-O distance of 1.30Å. Since then, innumerable other such complexes have been prepared, with other ligands, primarily phosphines and isocyanides, and other central metal ions, such as Rh[160] and Pt,[161] for example. All of these complexes are diamagnetic, and all at least formally correspond to either $d^8 \rightarrow d^6$ or $d^{10} \rightarrow d^8$ oxidative addition, as discussed in chapter 1. The bonding in these complexes has been much discussed,[2,162,169] but no notable conclusions have been reached.

The investigations outlined in the present chapter were prompted by the report by Vaska, et al.[163] of a symmetrical dioxygen adduct of cobalt, the first ever reported. Electronic spectroscopy has not seen much application in the study of symmetrically bound dioxygen complexes, primarily because the known complexes were of metal ions whose spectroscopy is characterized by rather high-energy transitions, as well as by a notable lack of published papers. We hoped that the spectrum of the cobalt complex would be readily interpretable, and our hopes

have been rewarded.

We have also studied the properties and reactions of cobalt phosphine complexes in general, to aid in the interpretation of the properties of the oxygen complex, and to help in the acquisition of insights into why the symmetrical structure is stable in this complex while all other known cobalt dioxygen complexes have the "end-on" structure discussed at length in chapter 4. Much of this work has already been presented in chapter 3.

Finally, we have investigated symmetrical dioxygen complexes of Rh and Ir, in an attempt to correlate their properties with those of the cobalt complex. We will also discuss the well-known peroxide complexes of metal ions in high oxidation states (notably Cr(VI)), which have similar structures and provide additional insights into the electronic structure of the symmetrical MO_2 unit.

Experimental

Preparation of Compounds

$[Co(2=phos)_2](ClO_4)_2$. A solution of 0.75 g of $Co(ClO_4)_2 \cdot 6H_2O$ in 15 ml of acetone was added under nitrogen to a solution of 0.65 g of 2=phos in 30 ml of acetone. The solution turned orange, and a yellow crystalline product began to form. After storage at 10°C for one hour, the solution was filtered under nitrogen. The bright yellow crystalline product was washed with methanol and ether. It is indefinitely stable in air when dry. The tetrafluoroborate was prepared similarly, from $Co(BF_4)_2 \cdot 6H_2O$, as bright

yellow crystals.

Analysis:

Calcd for $[Co(2\text{=}phos)_2](ClO_4)_2$: C, 59.22; H, 4.59; P, 11.75

Found: C, 58.62; H, 4.28; P, 11.72.

$[Co(2\text{=}phos)_2](BF_4)$. To a solution of 4.5 g of 2=phos and 4.0 g of $NaBF_4$ in 350 ml of refluxing ethanol under nitrogen was added 2.5 g of $CoCl(PPh_3)_3$ (prepared as an apple-green powder by the zinc reduction method of Aresta, et al.[164]). After refluxing for one hour, the solution was cooled in an ice bath for an hour. Filtration under nitrogen gave 3.5 g of glistening, dark green, crystalline product. (The product at this point contains impurities, mainly cobalt metal, which were present in the $CoCl(PPh_3)_3$, which is very difficult to purify. The product may be recrystallized from ethanol or CH_2Cl_2, but is extremely oxygen-sensitive.) Exposure of the green filtrate to air and addition of excess solid sodium tetraphenylborate gives the BPh_4^- salt of $Co(2\text{=}phos)_2O_2^+$ as a light brown powder (yield $\simeq$ 1 g) which may be purified as described below.

$[Co(2\text{=}phos)_2O_2]X$, where $X^- = ClO_4^-$, BF_4^-, BPh_4^-, or PF_6^-, was prepared by several different methods, as described below for $X^- = BF_4^-$.

a) Solid $[Co(2\text{=}phos)_2](BF_4)$ was dissolved in CH_2Cl_2 in the presence of air. The initially bright green solution rapidly turned dark brown. After filtration to remove gray powdery impurities, the solution was evaporated in a stream of air to give a partly

crystalline dark-brown solid. The solid was redissolved in methanol, the solution was filtered, and a large excess of a saturated solution of $NaBF_4$ in methanol was added. Storage at -5 °C overnight gave large, well-formed, dark brown plates of the product, which were filtered off, washed with cold methanol, and air-dried. The product could additionally be recrystallized from CH_2Cl_2 -benzene, but solvent molecules seemed to be present in the resultant crystals. This recrystallization procedure was useful for the tetraphenylborate, which was otherwise difficultly crystallizable, and which formed large, shiny, blunt needles from CH_2Cl_2-benzene.

b) Solid 2=phos (1.20 g) was added slowly to a solution of 0.50 g of $Co(BF_4)_2 \cdot 6H_2O$ in 20 ml of acetone, with dioxygen being constantly bubbled through the solution. Acetone was periodically added to maintain the solvent level. The solution changed color, through gold, to dark brown. After completion of the addition, O_2 bubbling was continued for one half hour. Ether was then added, precipitating a light brown product. The precipitate was filtered off and washed with benzene (to remove unreacted 2=phos and its decomposition products) and ether. The product (yield $\simeq$ 1g) was recrystallized as described in a).

c) $[Co(2=phos)_2](BF_4)_2$ (0.32 g) was dissolved in methanol (350 ml) and refluxed for one half hour, with air being constantly bubbled through the solution. The solution turned dark brown over 20 minutes. Reduction of volume in a stream of air gave

dark brown crystals of the product, with by-products of the reaction crystallizing when the solution was nearly dry. The product could be recrystallized as previously described. In one preparation, the product solution was refluxed for several hours and quantitatively diluted to 500 ml. Measurement of the absorbance at 476 nm indicated a yield of 50%, as described in the text.

Satisfactory elemental analyses were obtained for the oxygen complex for several different preparations and anions. Products from different preparations could also be readily compared by their electronic spectra.

$[Rh(2\text{-phos})_2]Cl$ was prepared by the method of Sacco and Ugo[165] and $[Rh(2\text{=phos})_2]Cl$ was similarly prepared. They could be recrystallized from methanol under nitrogen as their ClO_4^-, BF_4^-, or PF_6^- salts. The dioxygen adduct $[Rh(2\text{-phos})_2O_2]PF_6$ was prepared as brown crystals by the method of Ibers et al.[160] (This method is only sporadically successful, the unoxygenated complex often co-crystallizing.)

$[Ir(2\text{=phos})_2]Cl$ was prepared by G. Geoffroy. The O_2 adduct was crystallized (yellow rhombs) as the perchlorate salt $[Ir(2\text{=phos})_2O_2](ClO_4)$, from an O_2-saturated methanol solution of the Ir(I) complex.

Attempts were made to prepare the S_2 adducts of $Rh(2\text{-phos})_2^+$ and $Rh(2\text{=phos})_2^+$ by the method described for the

2-phos complex by Ginsberg and Lindsell.[166] Non-crystalline brown materials were obtained. Chloroform extraction of the crude product from the $Rh(2=phos)_2^+$ reaction gave a violet extract from which purple crystals of an unidentified complex could be obtained.

Spectroscopic Measurements

All measurements were done as described in previous chapters.

Results and Discussion

Complexes of d^6 Metal Ions

The complexes $Ir(2\text{-}phos)_2^+$ and $Rh(2\text{-}phos)_2^+$ form well-defined, isolable dioxygen adducts for which crystal structure determinations have been performed.[160] In the iridium complex, the O-O bond distance is 1.63Å, while in the rhodium complex it is 1.42Å. (These distances roughly correlate with the reversibility of the oxygenation reaction, which is facile for the rhodium complex and very slow for the iridium complex. We will comment on this in due course.) In contrast, $Co(2\text{-}phos)_2^+$ on exposure to air decomposes to give phosphine oxides, either in solution or in the solid state.[163]

However, Vaska et al.[163] recently communicated a study of the cobalt, rhodium, and iridium complexes of the unsaturated ligand 2=phos, and reported that all three $M(I)(2=phos)_2^+$ complexes formed stable dioxygen adducts. The crystal structure[167] of $Co(2=phos)_2O_2^+$, as the tetrafluoroborate salt, shows it to have the

same "oxidative addition" structure as the rhodium and iridium 2-phos complexes, with an O-O band length of 1.42Å. We have prepared the cobalt complex by a number of methods, including that employed by Vaska,

1) $$Co(2\text{=}phos)_2^+ + O_2 \rightarrow Co(2\text{=}phos)_2O_2^+$$

and find the complex to be extremely stable. Solutions in solvents such as acetonitrile show very minor decomposition (from electronic spectra) over several days. Exposure of the complex in aqueous ethanol to strong acids such as $HClO_4$ and HBF_4 causes no immediate spectral changes (implying that the basicity of the complexed O_2 unit is very low), the solutions decomposing over a few hours to give Co(II), with no detectable intermediates. (Hydrochloric acid gives, slowly, trans-$Co(2\text{=}phos)_2Cl_2^+$, the yield not being quantitative, however.)

The factors involved in the stability of this complex seemed rather obscure, and as one route of investigation, we decided to investigate the reactions of the cobalt(II) complex $Co(2\text{=}phos)_2^{2+}$. This complex is readily prepared as a tetrafluoroborate or perchlorate salt by anaerobic reaction of the appropriate cobaltous salt with the ligand in acetone, the bright yellow product crystallizing from the reaction mixture. The 2-phos analogue has been reported to have a magnetic moment of 2.50 B.M., and a conductivity consistent with a 1:2 electrolyte.[168] The infrared spectrum of the solid perchlorate salt gives no indication of coordination of the perchlorate anions, and there thus seems to be

little doubt that this is an authentic low-spin square planar cobalt(II) complex. (A considerable number of 5-coordinate adducts of complexing anions exist, some of which we employed as starting materials in the syntheses detailed in chapter 3.)

When the preparation is attempted aerobically, however, the solution turns dark brown and no product crystallizes. Work-up of the solution yields, surprisingly, $Co(2\text{=}phos)_2O_2^+$, in somewhat less than 50% yield based on starting materials, as well as a considerable amount of cobalt(II) and ligand decomposition products. (This procedure is a considerably simpler method of preparing the dioxygen adduct than that employed by Vaska, but results in considerable loss of the rather expensive phosphine ligand.)

Unsurprisingly (at this point), reaction of $Co(2\text{=}phos)_2^{2+}$ with O_2 in various solvents (methanol, acetonitrile, methylene chloride, etc.) also yields $Co(2\text{=}phos)_2O_2^+$. The reaction is quite slow and no intermediates can be observed spectrophotometrically. In a quantitative experiment in which we forced the reaction to completion, the absorbance of the product solution at the low-energy peak of the dioxygen adduct at 476 nm indicated a 50.5% yield (with an estimated uncertainty of about one percent.) Additionally, the absorbance at the intense ultraviolet peak of the dioxygen complex at 322 nm was consistent with a 53% yield, indicating that no other products absorbing strongly at this wavelength (such as another cobalt(III) complex or free phosphine

ligand) had been formed. (Absorbance at higher energies began to deviate strongly from the $Co(2\text{=}phos)_2O_2^+$ spectrum.)

Cyclohexane extracts of the residues obtained by evaporating reaction solutions to dryness have electronic spectra showing characteristic phenyl vibrational structure between 250 nm and 280 nm, and we infer that residual phosphine ligand is primarily present as phosphine oxides, there being little trace here (or in the original product solution) of the intense free phosphine $n \rightarrow \pi^*$ transition. Infrared spectra of the residues show strong P=O stretching bands. The residues (and also the original solutions) give a strongly positive qualitative test for Co(II) with thiocyanate.

We conclude that the reaction is a "disproportionation" reaction, with a reasonable mechanism (emphasizing the presumed similarity to the reactions of chapter 4) being as follows:

2) $$Co(2\text{=}phos)_2^{2+} + O_2 \rightleftharpoons Co(2\text{=}phos)_2O_2^{2+}$$

3) $$Co(2\text{=}phos)_2O_2^{2+} + Co(2\text{=}phos)_2^{2+} \rightarrow [Co(2\text{=}phos)_2]_2O_2^{4+}$$

4) $$[Co(2\text{=}phos)_2]_2O_2^{4+} \xrightarrow{\text{fast}} Co(2\text{=}phos)_2O_2^{+} + Co(2\text{=}phos)_2^{3+}$$

5) $$Co(2\text{=}phos)_2^{3+} \xrightarrow{\text{fast}} Co(II) + \text{oxidized phosphines}$$

(We have neglected possible solvent involvement in the various postulated intermediates shown.)

One way of looking at the reaction is as a formal disproportionation of Co(II) into Co(I) and Co(III), with O_2 stabilizing the Co(I) (by oxidizing it to Co(III) and forming a strong complex.)

The instability of the Co(III) product $Co(2=phos)_2^{3+}$ (which might be better represented as $Co(2=phos)_2(S)_2^{3+}$, where S is a solvent molecule) is consistent with observations in chapter 3 that indicated that this ion, as prepared by other methods, was apparently unstable. We related this instability to steric effects, and steric effects can also be used to rationalize the instability of the μ-peroxo intermediate. In order for this Co(III) complex to attain (distorted) octahedral coordination, solvent molecules must coordinate trans- to the peroxide group. (The μ-peroxo dimer of Co(salen) has solvent dimethylformamide molecules in these positions.[142]) This should be sterically unfavorable, and explusion of a solvent molecule, with the other end of the peroxide group coming in to coordinate, releasing the other Co(III) ion, seems reasonable. (It is clearly possible to eliminate the solvent molecules from the argument altogether. The reaction is then simply dissociation of one of the Co(III)'s from the bridging peroxide. Five-coordinate Rh(III)[172] and Ir(III)[192] complexes are known with bulky phosphines.) Similar arguments could be applied to the monomer, $Co(2=phos)_2O_2^{2+}$, to account for the slowness of the net reaction, the equilibrium constant of reaction 2) apparently lying far to the left. (It is conceivable that this might be a symmetrically bonded superoxide complex, of which there are no well authenticated examples, but this is purely speculative.)

The structure of $Co(2=phos)_2O_2^{+}$ is relatively unstrained because of the short O-O distance, the diphosphines being allowed

to expand out into the space left vacant. The P-M-P bond angles are observed to deviate from octahedral values by 5 to 10 degrees.[167] As best as one can guess, the oxidative instability of $Co(2\text{-phos})_2O_2^+$ can again be ascribed to the greater steric volume of the diphosphine $-(CH_2)_2$ moieties.

However, we are undoubtedly missing some interesting electronic effects if we attempt to ascribe all of the observed chemistry to steric effects. But before we consider this in more detail, we will first consider the electronic spectrum of $Co(2\text{=phos})_2O_2^+$.

In figure V-1 we show the electronic spectrum of $Co(2\text{=phos})_2O_2^+$, as the BF_4^- salt, in methanol solution at room temperature. The spectrum shows three absorption features, a shoulder at ~16 kK ($\epsilon \simeq 75$), a sharp peak at 21.03 kK ($\epsilon = 1020$), and an intense peak at 31.00 kK ($\epsilon = 17,800$). A broad feature at ~38 kK is ascribable to phenyl $\pi \rightarrow \pi^*$ absorption, with the very weakly structured higher energy portion of the spectrum being, as usual for aryl phosphine complexes, difficult to interpret.

The behavior of the spectrum at low temperature is shown in figure V-2. Note the very close agreement in room temperature energies and intensities with figure V-1, for a change of both solvent (to 12/1 EPA/$CHCl_3$) and anion (to PF_6^-). The peak at 21 kK at room temperature blue-shifts strongly at 77 °K, to 21.64 kK, and increases peak intensity slightly. A shoulder is discernable at ~26 kK ($\epsilon \simeq 1200$). The intense peak in the near

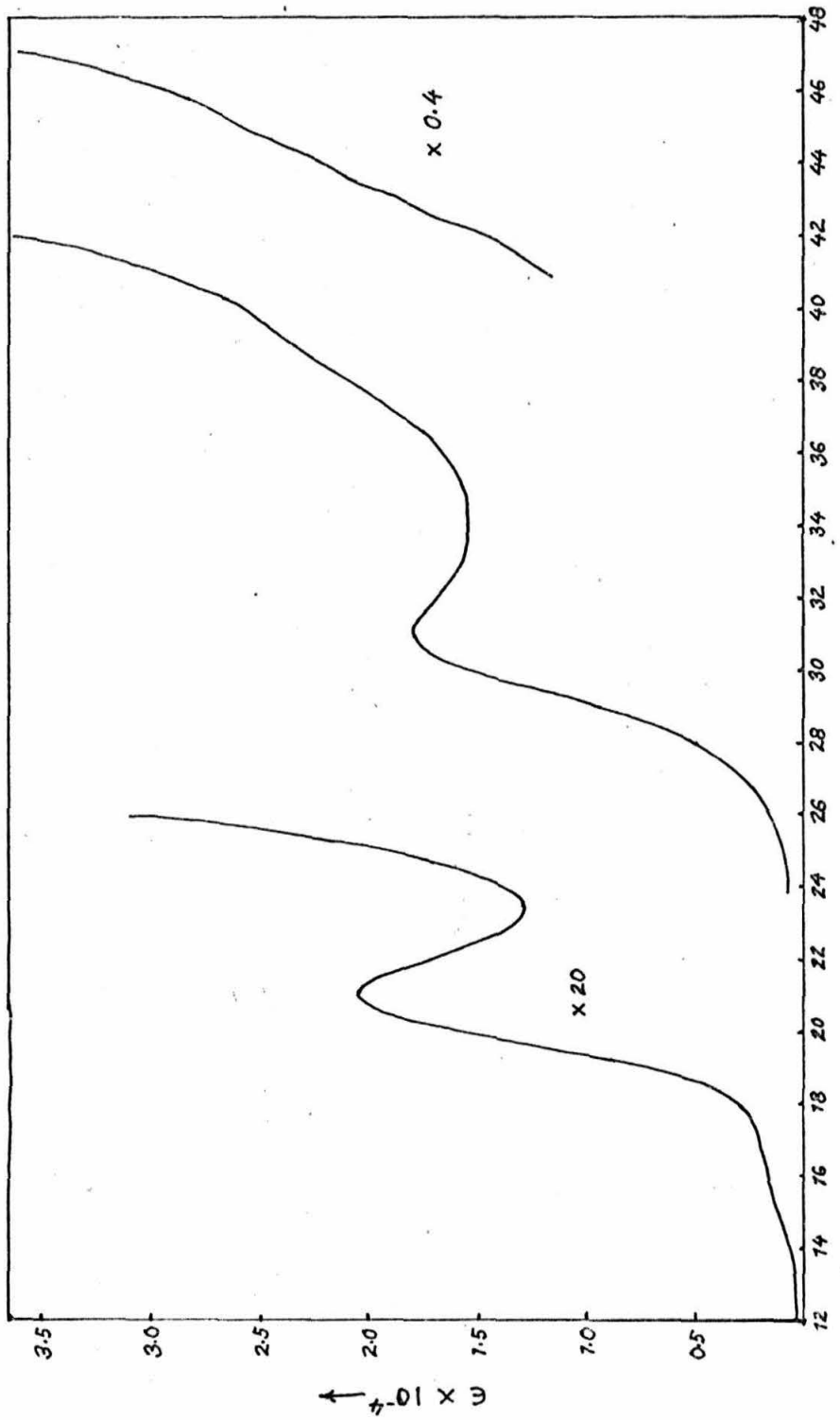
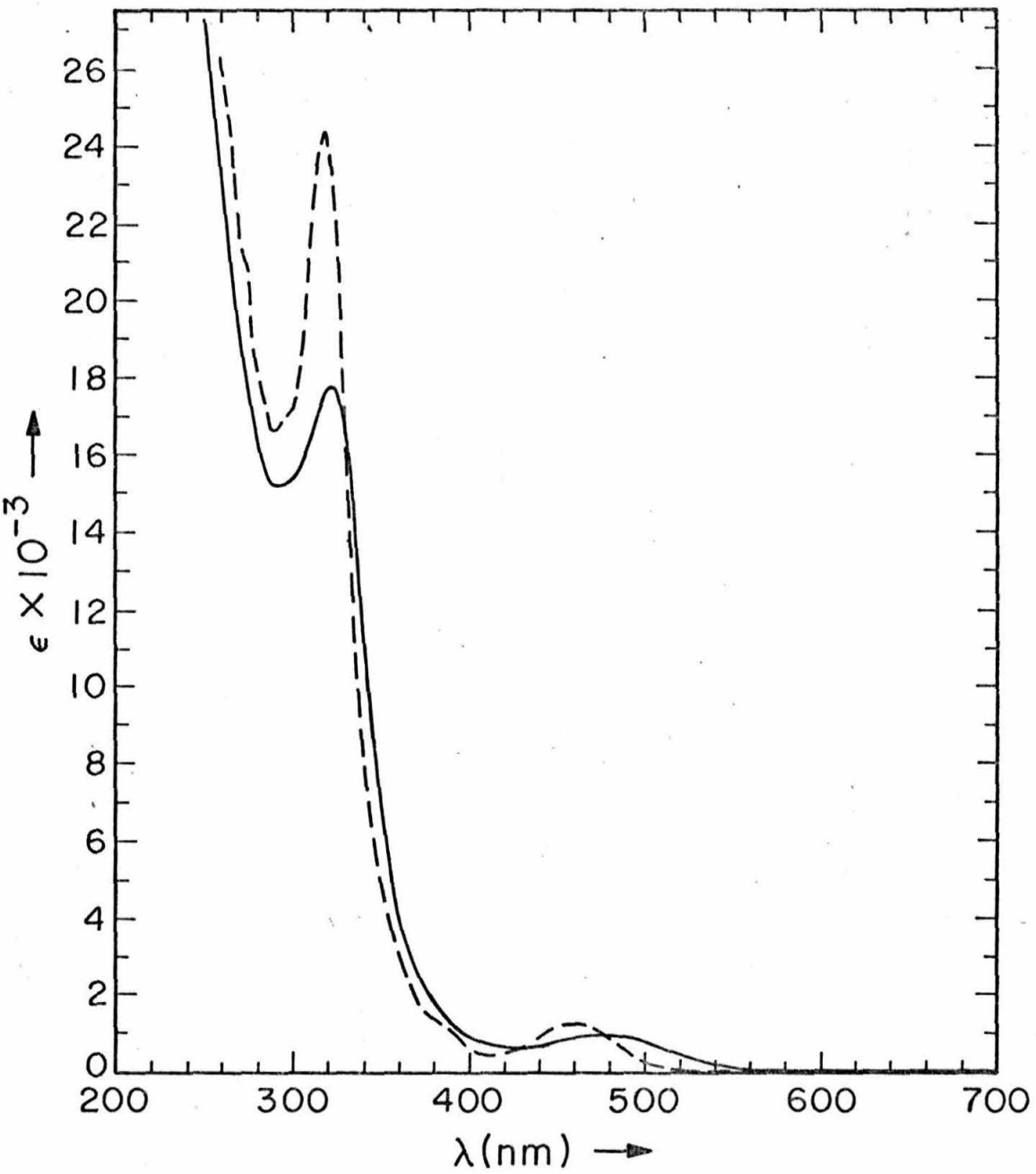


Figure V-1. Electronic spectrum of $[Co(2\text{=phos})_2O_2]BF_4$ in methanol, R.T.

Figure V-2. Electronic spectra of $[Co(2\text{=}phos)_2O_2]PF_6$ in 12:1 EPA:$CHCl_3$ at R.T. (——) and 78°K (----).


26
24
22
20
18
16
14
12
10
8
6
4
2
0
ε X 10^-3
200
300
400
500
600
700
λ(nm)

ultraviolet sharpens and intensifies considerably, and shifts moderately to higher energy to 31.35 kK. Finally, the phenyl transition at higher energy shows increased resolution into individual vibronic transitions.

For the interpretation of the spectrum, we place heavy reliance on the material presented in chapter 3. We initially remark that the spectrum is most definitely not that of a Co(I) or Co(II) complex. Co(I) complexes have intense low-energy ligand field transitions, the lowest energy being at 13.5 kK (ϵ = 1300) for the square planar, low-spin $Co(2=phos)_2^+$,[163] and show no charge-transfer bands below 50 kK. Co(II) complexes similarly show very low-energy transitions (which are often structured), the square pyramidal $Co(2\text{-phos})_2Cl^+$ having bands at 16.7 kK (ϵ = 600), 14.7 kK (ϵ = 730), 0.72 kK (ϵ = 120), and 0.48 kK (ϵ = 80).[73] (We should note that $Co(2=phos)_2O_2^+$ shows no absorption other than ligand vibrational overtones in the near infrared.)

On the other hand, the observed spectrum is exactly that expected for a cis-disubstituted cobalt(III) phosphine complex. The intense band at 31 kK is at nearly the same energy (and is of comparable intensity) to the phosphine-to-cobalt(III) charge-transfer bands discussed in chapter 3, the best comparison being to the cis-dichloro complex mentioned at the end of that chapter.

As to ligand field transitions, cis-$Co(en)_2(OH_2)_2^{3+}$ has its $^1A_1 \rightarrow$ "$^1E^a$" transition at 20.9 kK, and a shoulder at ~25 kK, assignable to the "$^1A_1 \rightarrow {}^1T_2$" transition.[38] (cis-$Co(en)_2Cl_2^+$) has

a definite maximum at 25 kK.) The band at 21 kK in the spectrum of $Co(2=phos)_2O_2^+$ can thus be assigned to the $^1A_1 \rightarrow {}''^1E^a{}''$ ligand field transition, the intensity of the transition being due to the strong distortion from octahedral symmetry, among other factors, as discussed in chapter 3. The energy of the transition implies that symmetrically bound O_2^{2-} has a ligand field strength closely comparable to that of cis-$(OH_2)_2$, and, keeping in mind the correlations of chapter 3, perhaps somewhat lower than cis-$(OH_2)_2$. The spectrochemical properties we derive for end-on bound peroxide (discussed in chapter 4) and symmetrically bound peroxide are thus very similar, with the best interpretation of the slightly lower ligand field strength of symmetrically bound peroxide being that it is a stronger π-donor (vide infra). The shoulder observed at low temperature at ~26 kK is readily assigned as the $''^1A_1 \rightarrow {}^1T_2''$ ligand field transition.

The assignment of the weak shoulder at ~16 kK is somewhat more obscure. An assignment to the $^1A_1 \rightarrow {}''^1A_2''$ ligand field transition was considered, as this transition should be weak, but the implied splitting of the octahedral $^1T_1$ state seems too large. Alternatively, the shoulder may be a singlet-to-triplet ligand field transition, or perhaps even a very forbidden charge-transfer band. Attribution to impurities seems ruled out by its presence in many different preparations of the complex.

We do not observe any bands which can be assigned to peroxide-to-metal charge-transfer, very much in contrast to the

"end-on" peroxide complexes. This cannot be due to considerations as transitions to the cobalt(III) dσ orbital ("$d_{x^2-y^2}$") involved in σ-bonding are formally allowed from both the π* in-plane σ-bonding orbital ($^1A_1 \rightarrow {}^1A_1$) and the π* out-of-plane π-bonding orbital ($^1A_1 \rightarrow {}^1B_2$) in C_{2v} symmetry. It is possible (and probable) that one or more of these transitions is part of the unresolved absorption at greater than 35 kK. The two charge-transfer transitions observed for $[Co(NH_3)_5]_2O_2^{4+}$ at 34.5 kK and 27.8 kK were rather weak ($\epsilon \sim 3000$), and an additional possibility exists (again, probable) that one or more of the expected charge-transfer transitions is hidden under the intense phosphine charge-transfer. Recalling our arguments on the assignment of the assignment of the charge-transfer transitions in $[Co(NH_3)_5]_2O_2^{5+}$, which also has the π* orbitals strongly split, it is additionally conceivable that the π* out-of-plane → dσ* transition might be rather weak and low-energy, and that one of the three bands at lower energy might be this transition. This is, again, speculative. Our principal conclusion on symmetrically-bound-peroxide Co(III) charge-transfer is that intense low-energy transitions are not observed.

In figure V-3 we show the electronic spectrum at room temperature and 77 °K of $Ir(2\text{-phos})_2O_2^+$, which we investigated for comparison. As all bands are blue-shifted and ligand absorbance is considerable, we cannot be particularly definite in our assignments. The shoulder at 33-34 kK ($\epsilon \simeq 5000$) is assigned as the $^1A_1 \rightarrow {}^1E^a$" ligand field transition, the shift to higher energy of

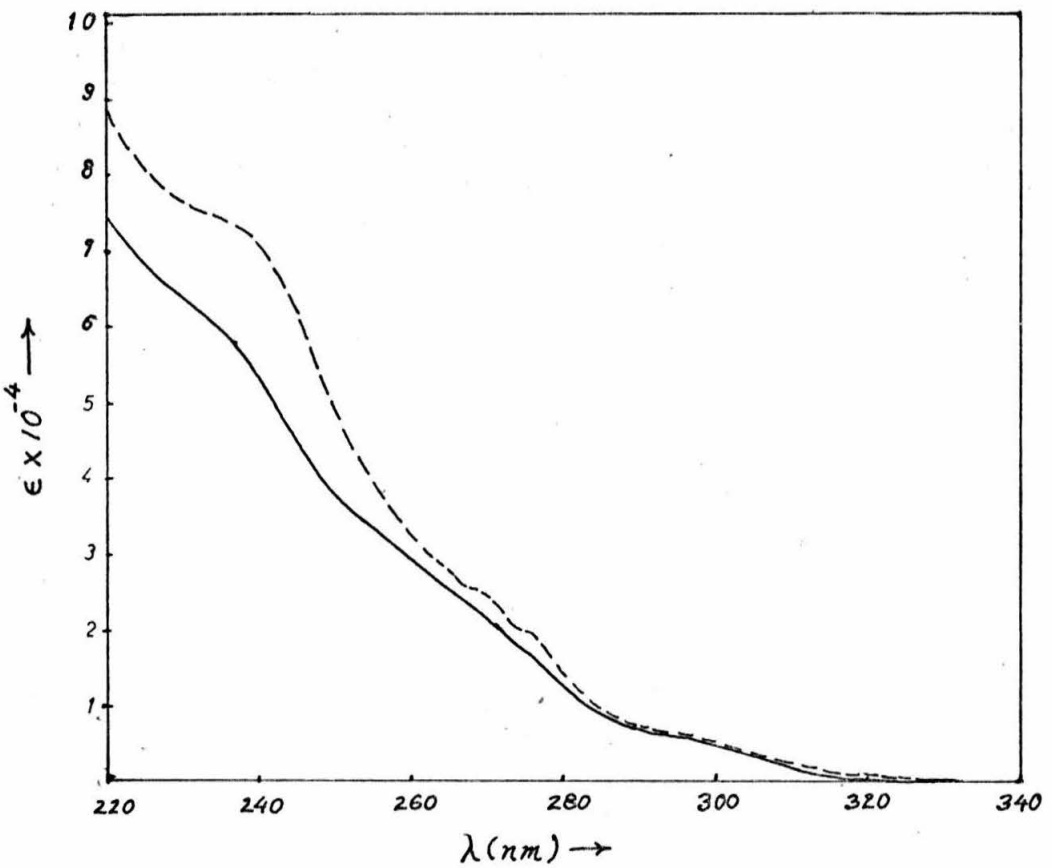


Figure V-3. Electronic spectra of $[Ir(2\text{=}phos)_2O_2]ClO_4$ in EPA at R.T. (——) and 78°K (----).

~12 kK relative to the cobalt complex comparing favorably to the shifts observed for other iridium complexes. (The lowest energy ligand field transition in trans-$Ir(en)_2Cl_2^+$, for example, is blue-shifted by 12.6 kK[170] from the transition in trans-$Co(en)_2Cl_2^+$.) A singlet-to-triplet transition should be observable at lower energies in the iridium complex, and we made a search for it, but found that the oxygenation reaction is apparently not completely reversible, very small concentrations of $Ir(2\text{=}phos)_2^+$ being present in concentrated $Ir(2\text{=}phos)_2O_2^+$ solutions. The absorption bands of the Ir(I) complex, which have very high ϵ's, showed up as very weak shoulders in the visible, and made it impossible to locate triplet bands with any certainty.

Particularly at 77°K, a shoulder at ~43 kK ($\epsilon \simeq 70,000$) is very evident, and has no obvious counterpart at the same energy in the spectrum of $Co(2\text{=}phos)_2O_2^+$. The energy seems reasonable for phosphorus-to-Ir(III) charge-transfer, by arguments similar to those used for the ligand field band.

Comparison to the spectrum of $Rh(2\text{=}phos)_2O_2^+$ would be instructive, as the rhodium complexes are generally very reversible, and if any case of dioxygen complexation without oxidative addition occurred, it might be here. Unfortunately, the equilibrium constant of the oxygenation reaction lies to the left in solution and we could not isolate any pure solids. The complex $Rh(2\text{-}phos)_2\text{-}O_2^+$ can be isolated, by the method of Ibers, et al.,[160] but satisfactory spectral data could still not be obtained, as dissolution

in any solvent or preparation of a KBr pellet reversed the oxygenation reaction, while mull spectra gave extremely poorly resolved spectra, of little interest. (The complex is brown, and mull spectra show relatively featureless rising absorption. Some weak features are observed, but we were not entirely sure of the homogeneity of any of our samples, and decline to comment further.) Difference spectra methods employed on the complex in solution indicate with some certainty an intense band at ~280 nm, and this might be assigned to the expected phosphine charge-transfer transition. The estimated intensity of the band, based on decreased Rh(I) absorption at lower energy, seems crudely reasonable for this assignment, as is the observed energy. The intense absorption of the Rh(I) complex made it impossible to detect a ligand field band.

Some rhodium dioxygen complexes are stabler, but data in the literature[171,172] do not allow any sensible conclusions. The orange-red complex $(Rh(OCOCF_3)(CO)(O_2)(PPh_3)_2$ is reported to have a band at 424 nm ($\epsilon = 7700$)[172] which might be a ligand field transition, but the ligands other than O_2 in the complex are a bit too varied to allow much to be made of this.

Finally, we have attempted to study the S_2 adducts reported by Ginsberg and Lindsell.[166] The crystal structure of the $Ir(2\text{-phos})_2^+$ adduct has been reported, and reveals a geometry suggestive of an S_2^{2-} complex, with an S-S bond distance of 2.07Å. We concentrated on the rhodium complex, which we expected to have a more interesting spectrum than the iridium complex.

A solution of S_8 and $Rh(2\text{-phos})_2^+$ in benzene-ethanol rapidly darkens over several days, and orange-brown solids may be isolated, and recrystallized as perchlorates (although the crystallinity of the products is more inferred than observable). The solution electronic spectrum is quite uninteresting, showing only a broad, rising, absorption tail. We admit, of course, that we are not at all certain that we prepared the desired complex. Interestingly, the reaction of $Rh(2\text{=phos})_2^+$ with S_8 is very slow, and it was necessary to reflux a solution for five days before most of the $Rh(2\text{=phos})_2^+$ was observed to have reacted. Work-up of the products yielded no compounds likely to be an S_2 adduct, with the single crystalline complex that was isolated being purple. (Other products were brown, amorphous, and intractable.)

Our investigation of the electronic spectroscopy of symmetrically bonded dioxygen complexes provides strong evidence for considering the complexes as containing peroxide bound to trivalent (low-spin d^6 metal) ions. Some independent evidence exists for characterization of the O_2 groups as peroxide ligands. $Co(2\text{=phos})_2O_2^+$ has a strong O-O infrared stretching frequency at 909 cm^{-1} in chloroform solution, the band splitting into a doublet at 908 cm^{-1} and 899 cm^{-1} in the solid BF_4^- salt. $Rh(2\text{=phos})_2O_2^+$ and $Ir(2\text{=phos})_2O_2^+$ have the corresponding stretches at 876 cm^{-1} and 845 cm^{-1} in $CHCl_3$.[163] The energies are clearly characteristic of O-O single bonds. The observed variation along the series Co, Rh, Ir is perhaps most closely related to the increase in M-O

distances along this series. The O-O distances do not closely correlate with stretching frequencies, nor do they correlate closely with the reversibility of the oxygenation reaction, when the central metal ion is varied. Thus, $Rh(2\text{-phos})_2O_2^+$ and $Co(2\text{-phos})_2O_2^+$ have nearly the same O-O distance (1.42Å[160,167]), but vastly different tendencies to revert to starting materials. (Incidentally, $Ir(2\text{-phos})_2O_2^+$[163] and $Ir(2\text{-phos})_2O_2^+$[174] have identical O_2 stretching frequencies.) Both O-O distances and O-O stretching frequencies are clearly subject to variation as a function of M-O distance and the resultant variation in energetic dependence on O-M-O bond angle deformation.

The variability of O-O bond distances in complexes of the type $O_2IrX(CO)(PPh_3)_2$ as a function of X^- is somewhat more conclusive. The bond distances vary from 1.53Å[175] to 1.36Å[167] to 1.30Å[159] along the series I^-, Br^-, Cl^-, and this variation correlates directly with the reversibility of the reaction, deoxygenation of the chloro complex being facile, while deoxygenation of the iodide is not. It clearly also correlates with the π-donor strength of X^-.

We attribute the effect to π-donation of the coordinated peroxide group. Such π-donation leads to a formal increase in O-O bond order, which should be reflected in a shortening of the O-O bond distance, and should correspondingly lead to a reduction of the activation energy for O_2 release. The direct cause of variation in the π-donor interactions of the peroxide is the variation

of π-donor strength of X^-. The strong π-donor interaction of iodide produces a metal center which is more electron-rich than the chloride complex, with a resultant decrease in π-donation from peroxide. (Note that these interactions continue to be considered as a perturbation upon an Ir(III)-peroxide complex.)

For π-donor interactions to be as important as we are suggesting is somewhat unusual for a low-spin d^6 complex. The key factor here is undoubtedly the phosphine ligands and their π-acceptor capacity, discussed in chapter 3. The M(I) complexes are stable precisely because of π-acceptor bonding of the phosphines, which reduces the electron density on the metal ions. Co(I) complexes are <u>only</u> known with strong π-acceptor ligands such as phosphines and carbon monoxide. We noted in chapter 3 that π-donor ligands lent stability to Co(III) phosphine complexes. The effect in our formulation is a synergistic one, with the phosphines depleting $d\pi$ electron density and π-donor ligands replenishing $d\pi$ electron density. We emphasize that the effect occurs in the $d\pi$ orbitals. On formation of a complex, electrons originally present in antibonding metal $d\sigma^*$ orbitals are transferred to O_2 π^* orbitals, and are, in a sense, then pumped back into the metal ion to some extent, but <u>not</u> into the $d\sigma^*$ orbitals. (<u>Sigma</u>-donation <u>is</u>, of course, donation into $d\sigma^*$ orbitals, but is quite another process, and probably has little to do with O-O bond distance variation.) The spectroscopic oxidation state of the metal ion thus remains low-spin d^6 M(III).

The very low tendency of $Co(2=phos)_2^{2+}$ to react with O_2 is now readily rationalized. The effect of the phosphines is to produce a rather low (for a cobalt(III) complex) electron density on the central metal ion, decreasing the reducing strength of the ion. Furthermore, the dioxygen complex will be destabilized, as an end-on (or even symmetrically bound) superoxide ligand is a relatively weak π-donor. (The suitability of end-on bound peroxide as a ligand in phosphine complexes is unclear, as no good examples have been reported. Complexes of the type $IrX(OOBu\text{-}\underline{t})_2(CO)L_2$ of tert-butyl hydroperoxide have been reported,[176] but have not been investigated in detail. We would presume that these complexes should be stable on electronic grounds, but, at least for Co(III), might be destabilized by steric effects.) The symmetrically bound peroxide complex, however, which has the advantages of utilizing the full π-donor capacity of the peroxide group and having a minimum of steric hindrance because of the small size of the "chelating" peroxide group, is quite stable. Just as for the $Co(2=phos)_2X_2^+$ complexes discussed in chapter 3, a combination of electronic and steric arguments thus account fully for the observed stability patterns. The arguments employed here are closely related to those we used in the discussion of cobalt Schiff base complexes in chapter 4. The distinction is presumably that the Schiff base ligands are weaker π-acceptors, with the planar steric constraint of the Schiff bases also perhaps being of importance.

We have arrived at the conclusion that the dioxygen adducts formed by d^8 metal complexes are d^6 complexes of peroxide ligands, and have shown that the peroxide ligands are both strong σ-donors (to account for their moderate ligand field strength) and strong π-donors. It would logically follow that peroxide ligands should stabilize high metal oxidation states, despite the reduction potential of peroxide. Such is, in fact, the case.

Complexes of Metal Ions in High Oxidation States

Peroxide complexes are known for virtually all metal ions that possess stable high oxidation states. A partial list includes Cr(VI), Mo(VI), W(VI), V(V), Nb(V), Ta(V), Ti(IV), Zr(IV), Hf(IV), Th(IV), and U(VI).[18,177,178,179,180,181] We will concentrate on the chromium complexes which have been well characterized structurally.

Treatment of pyridine-water solutions of CrO_3 with hydrogen peroxide[182] gives the purple compound $CrO(O_2)_2py$. (In neutral or acidic aqueous solution, explosive salts of the ion $CrO(O_2)_2(OH)^-$ can be obtained.[183]) The crystal structure of the pyridine complex[184] shows it to be approximately a pentagonal pyramid with an oxide oxygen at the apex and two symmetrical peroxides and a pyridine coordinated equatorially, with a peroxide O-O distance of 1.40Å. The purple color is due to a band in the visible, which in benzene at room temperature[178] is split into two components at 580 nm and 730 nm. The ϵ's are about 500. Derivatives with ligands other than pyridine, such as ethers or 1,10-phenanthroline,

have very similar spectra.[178,183] At higher energy in complexes of ligands which do not have intra-ligand transitions, an intense band is observed at 210 nm ($\epsilon \simeq 6000$).[179]

These diamagnetic[183] compounds are clearly best considered to be Cr(VI) complexes. The comparison to all the other peroxide complexes of high oxidation state metal ions is particularly suggestive in this regard, but additional evidence exists in that peroxide complexes of Cr(V) and Cr(IV) can also be prepared. The (d^1) Cr(V) complex is the dodecahedral $K_3[Cr(O_2)_4]$,[186] which has one unpaired electron and two weak ($\epsilon \simeq 50$) bands in the visible (17 to 18 kK) which are probably d-d transitions. (The d^0 V(V) complex $K_3[V(O_2)_4]$ is reported to be isomorphous with the chromium complex.[177,186] Cr(IV) complexes of the form $Cr(L)_3(O_2)_2$, where L is, e.g., NH_3, can also be isolated,[185] and have two unpaired electrons, as expected for a d^2 system, and a pentagonal bipyramidal structure, with two of the L groups axial and one equatorial. These complexes have[185] three weak bands ($\epsilon \simeq 20$ to 30) in the visible between 500 and 600 nm, which, again, can be assigned as d-d transitions, and also have a band at 360 to 370 nm ($\epsilon \simeq 500$) and one at ~250 nm ($\epsilon \simeq 5000$) which are assignable as charge-transfer transitions from the peroxide groups, the weaker band at lower energy presumably being the transition from the π^* out-of-plane (π-bonding) orbital. (As the symmetries of these complexes are rather low, no attempt will be made to assign the d-d bands in detail.) All of these chromium complexes incidentally, can be prepared from CrO_3 plus H_2O_2 in the presence of appropriate

ligands, more manipulations of the solutions being required than for the preparation of Cr(VI) complexes, however.

We consider the peroxide-metal bonding in these compounds to be entirely analogous to that in the compounds considered in the previous section. These compounds show no obvious tendency to dissociate O_2, but this is entirely explicable in terms of the instability of the metal complex which would be formed by such dissociation (leading to high activation energies). The reduction of the metal ions in peroxide solutions, which does occur on heating, probably occurs by a series of one-electron steps. (However, $CrO(O_2)_2 \cdot$ (diethyl ether) has been reported to be a source of what might be singlet dioxygen.[187]) In connection with this, Samuni[188] has reported the e.s.r. detection of superoxide complexes of Ti(IV) and V(V) as transients in solution.

Steric considerations are likely to be of secondary importance in these complexes, particularly in the case of the d^0 systems. $CrO(O_2)_2py$ can, in fact, profitably be considered to be pseudo-tetrahedral,[179] viewing the peroxide groups as single units, which suggests that the structure is primarily determined by electrostatic considerations, as in tetrahedral CrO_4^{2-}. The 2,2-bipyridine complex $CrO(O_2)_2(bipy)$ is distorted octahedral,[184] showing the flexibility of the coordination geometry.

Cr(VI) (and also Cr(V) and Cr(IV)) is only stable in complexes of strongly π-donating ligands, primarily oxide and halides. (We do not mean to slight the importance of strong

σ-donation, which is clearly also necessary, but only mean to emphasize that σ-donation is not sufficient to stabilize the complexes.) The stoichiometry of $CrO(O_2)_2(OH)^-$, which has no tendency to deprotonate in basic solution[183] (in contrast to $CrO_3(OH)^-$), suggests that symmetrically bonded O_2^{2-} is even a stronger π-donor than oxide, which is not unreasonable. CrO_4^{2-} has its lowest observed electronic transitions (in aqueous solution) at[189,192] ~435 nm (very weak) and 373 nm ($\epsilon = 4,600$), both being assigned to singlet-singlet charge-transfer transitions from a non-bonding oxide π level of t_1 symmetry to the vacant metal e level.[190,192] (Transitions from bonding π levels and σ levels are observed at higher energy.) The bands observed for $CrO(O_2)_2py$ at 580 nm and 730 nm can be assigned, very similarly, to transitions from peroxide π* out-of-plane (the CrO_2 plane) levels, the low symmetry of the complex not allowing as simple a group theoretical classification as for CrO_4^{2-}. The relatively low energy of the transitions is in keeping with our observations of low-energy (for Co(III)) charge-transfer transitions for peroxide complexes in chapter 4. (The presumably much greater π-bonding in the d^0 systems does not allow very direct comparisons of the charge-transfer energies.) The transition at 210 nm ($\epsilon = 6000$) is probably from the σ-bonding π* in-plane level. The high energy of this transition shows, of course, that O_2^{2-} is also a very strong σ-donor in these complexes.

This concludes our investigations of small molecule dioxygen complexes. We find that, essentially without exception,

these complexes can be sensibly viewed as dioxygen anion complexes of metal ions, the partitioning of the electrons generally being in keeping with expectations based on "stable" d configurations (d^0, d^3, d^6, d^8) and dioxygen anions (O_2^{2-}). Using this as firm ground upon which to view more subtle electron "bookkeeping" effects, we have been able to build a consistent representation of the properties of oxygen ligands and oxygen complexes. In the last chapter of this thesis, we will consider applications of these insights to metal ion-dioxygen systems for which we have much less information than those considered thus far.

CHAPTER VI

Inaccessible Dioxygen Complexes: Reaction Intermediates and Oxymetalloproteins

Introduction

The metal ion-dioxygen complexes we have discussed thus far are all distinguished by being stable in a kinetic sense. They are isolable, easily characterized substances, which have at most only one rapid reaction under the conditions of preparation and study, the reverse of the oxygenation reaction. The best examples we have of dioxygen complexes are those of Co, Rh, and Ir, and their stability can be attributed to the kinetic inertness of a low-spin d^6 configuration. Thus, dissociation of peroxide or superoxide is slow, while dissociation of O_2 might be fast.

Despite the stability of these complexes, Co, Rh, and Ir complexes are not important in biological dioxygen metabolism. This is actually not surprising from an evolutionary point of view. Dioxygen storage and transport is unnecessary in living organisms of less than some size and level of complexity which is well above the unicellular level. It seems obvious that chemical systems involved in reduction of dioxygen and utilization of the energy thereby released must have developed first, with the specialized metalloproteins that form long-lived, reversible dioxygen complexes being later developments of "advanced" organisms. Modification of already existing metalloproteins would have been

the simplest route to such proteins. Cobalt complexes, for example, are remarkably poor choices for use in dioxygen redox reactions, precisely because of the kinetic inertness of the Co(III) state, and the biological choice of iron and copper for its dioxygen metabolism machinery is thus readily understandable.

This nevertheless presents us with a considerable problem. "True" models for these proteins would be small molecule iron and copper dioxygen complexes. Unfortunately, there are no good examples of such complexes, primarily because iron and copper ions have efficient redox chemistries with dioxygen, the oxidized metal ions being not at all kinetically inert. We have adopted the viewpoint that the chances of obtaining suitable model complexes are rather low. (Such complexes are clearly not impossibilities, since nature seems to manage extremely well. However, the site engineering of a metalloprotein may be quite difficult to duplicate in a small molecule.)

In this chapter, we will, firstly, consider kinetic information which is available from study of the autoxidation reactions of iron and copper ions, and will summarize such conclusions as may be reached as to the nature of intermediate dioxygen complexes. We will then go on to discuss the oxymetalloproteins, and summarize the progress which has been made in pursuit of an understanding of their electronic structure.

Discussion

Autoxidation Reactions

The reaction mechanisms of metal ion autoxidations (oxidations by molecular oxygen) are in no case well established. This is not so much a problem of a lack of investigation as of inherent complexity, reflected in a tremendous variety of observed rate laws under different conditions. We wish to make inferences as to the structure of dioxygen complexes presumed to be intermediates in these reactions, and, as always for kinetic information, our conclusions are severely limited by the inherent restriction of information to, primarily, the stoichiometry of the net reaction and the stoichiometry of the rate-limiting step. We are assured neither of the presence of a dioxygen complex in this step, nor of the nature of any succeeding reactions, nor even that two stoichiometrically similar reactions which have very different rate laws have, indeed, different mechanisms. All of the discussion in this section, therefore, carrys with it an implied warning of caveat emptor.

Study of the autoxidation reactions of Cu(I) has been made difficult by the paucity of suitably soluble Cu(I) complexes, with instability with respect to disproportionation to Cu(II) and Co(0) being a constant problem. A recent study by Gray[197] of the autoxidation of Cu(I) in mixed $HClO_4$-CH_3CN-H_2O solutions seems, however, to have put the subject on fairly firm ground. The observed kinetics are:

1) $$\nu = k[Cu(CH_3CN)_2^+][O_2][H^+][CH_3CN]^{-2}$$

consistent with a proposed mechanism as follows:

2) $$Cu(CH_3CN)_2^+ \rightleftharpoons Cu^+ + 2CH_3CN$$

3) $$Cu^+ + O_2 \rightleftharpoons CuO_2^+$$

4) $$CuO_2^+ + H^+ \xrightarrow{\text{r.d.s.}} Cu^{2+} + HO_2$$

5) $$Cu^+ + HO_2 \xrightarrow{\text{fast}} Cu^{2+} + HO_2^-$$

6) $$H^+ + HO_2^- \rightleftharpoons H_2O_2$$

Close to a stoichiometric yield of H_2O_2 is observed, consistent with reaction 5). Hydroxyl radicals could <u>not</u> be detected, which tends to eliminate reaction 7):

7) $$Cu^+ + O_2 + H^+ \rightarrow Cu^{3+} + HO_2^-$$

as a possibility, since Cu(III) has been reported to react with water in acidic solution to give $\cdot OH$.[201]

The prime question is, how do we formulate the intermediate CuO_2^+? It can be formulated as a d^8 complex which happens to <u>dissociate</u>, upon protonation, to d^9 Cu(II) plus HO_2, but, lacking any evidence in favor of such a formulation, we prefer the simpler one of a Cu(II)-superoxide complex. Protonation of the complex is the rate-limiting step--that is, protonation is <u>not</u> fast, relative to other reactions, which is reasonable for a bound superoxide ion. (It could also, of course, be reasonable for a symmetrically bound peroxide.) There are several possible reasons why the reaction of O_2 with Cu^+ might be a $d^{10} \rightarrow d^9$ oxidative addition, while the

reaction of O_2 with Ni(0), Pd(0), and Pt(0) complexes gives (stable) M(II) complexes, e.g., $d^{10} \rightarrow d^8$ oxidative addition. Cu(III) is an intrinsically less stable oxidation state than, say, Pt(II), as implied by its reaction with water. (It is not even entirely clear that Cu(III) coordinated solely by oxygen donors would be low-spin, and a high-spin complex would have nothing at all to recommend it.) Without a stable "energy-well" such as a kinetically inert low-spin d^8 complex, there is no reason at all to expect a stable monomeric dioxygen complex. The known stability of d^9 Cu(II) clearly suggests it as the probable oxidation state in the transient complex. (Fortunately or unfortunately, the complete lack of model monomeric complexes, even in biological systems, prohibits any test of this argument. The formulation of the intermediate is thus a sort of theological problem. The only important point is that dissociation of superoxide leaves a stable, and labile, oxidation state, and that this is exactly what is observed. Incidentally, protonation of a bound superoxide would remove much of its bonding to a metal ion.)

The only remaining question is that of a monomer versus a dimer. Proton-assisted release of superoxide is a "reasonable" reaction mechanism, but an alternative reaction scheme involving formation of a dimer and direct release of peroxide is also, a priori, reasonable. (A "dimeric" mechanism involving an intermediate such as that shown in reaction 8)

8) $$2Cu^+ + O_2 \rightarrow [Cu\text{-}O_2\text{-}Cu]^{2+}$$

is possible even for an observed kinetic first-order $[Cu^+]$ dependence, but the detailed concentration dependencies observed by Gray[197] over a wide range of concentrations make such a mechanism seem at least very improbable in this case.)

If the monomeric intermediate is really a Cu(II)-O_2^- complex, then the observed kinetics are probably largely determined by the lifetime of the monomer, as reaction of the monomer with another Cu^+ should be thermodynamically favorable. The cobalt complexes discussed in chapter 4 show no tendency to release superoxide from monomers, and observed decomposition reactions are invariably from dimers. A major factor here is undoubtedly that reaction of a cobalt monomer with another Co(II) is not limited by dissociation from cobalt(III), whereas decomposition of a monomer is. An additional factor may be the negative charge on the unbound end of the superoxide in a monomeric metal ion-dioxygen complex, the fast rate of Cu(I) autoxidation perhaps implying the charge to be rather large. (The nearly full $d\sigma^*$ shell of a d^9 metal ion might have such an effect.) Extension of kinetic data to high pH's in search of dimer terms would be of interest, but the cuprous systems are unfortunately increasingly unstable at higher pH's.

Actually, a second-order dependence on $[Cu^+]$ has been reported[200] for the reaction of $CuCl_2^-$ with O_2 in glacial acetic acid, and the kinetics are reported to show no acid dependence, added CH_3SO_3H having no effect on the rate. (In contrast,

autoxidation of $CuCl_2^-$ in aqueous HCl has been reported to depend on $[H^+]$.)[198] A peroxo-bridged intermediate is at least suggested by the results. The effect of complexing anions and a non-aqueous solvent is obscure enough that we have no wish to attempt to explain the effect. Neither do we wish to attempt to explain observations by Zubermuhler[199] of Cu(I) autoxidations in the presence of NH_3 or imidazole proceeding with rates first-order in $[Cu^+]$ but without pH dependence (except to note that proton or hydrogen abstraction from complexed nitrogen base ligands is not completely implausible.) We mention additional results primarily to emphasize that the mechanistic situation is not as well established as our opening example might indicate, which is a proper note upon which to begin consideration of iron(II) autoxidation.

In acidic perchlorate solutions, the autoxidation of Fe(II) is a rather slow reaction (much slower than Cu(I) autoxidation), and proceeds with a rate law[203]:

9) $$\nu = k[Fe^{2+}]^2[O_2]$$

In neutral solution, the reaction is much faster, and a completely different rate law,[202]

10) $$\nu = k[Fe^{2+}][O_2][OH^-]^2$$

is followed. In acidic sulfate solutions a rate law[205]

11) $$\nu = k_1[Fe^{2+}][O_2] + k_2[Fe^{2+}]^2[O_2]$$

is observed, both reaction paths being accelerated by increasing sulfate concentration, the pathway which is first-order in $[Fe^{2+}]$

to a larger extent. Strongly complexing anions such as chloride strongly accelerate the first-order reaction path.[205]

The reaction thus seems to be entirely different from cuprous autoxidation. Not only is the characteristic reaction at low pH's second-order in $[Fe^{2+}]$, but the first-order pathway observed is quite distinctly not first-order in $[H^+]$. We will consider the second-order pathway first.

Rather than consider the aqueous system directly, we will consider a non-aqueous system. Dipyridine iron(II) porphyrins react with O_2 in benzene-pyridine solvent with kinetics which are complicated by dissociation of pyridine from the low-spin d^6 dipyridine complexes (producing reaction high-spin intermediates) being a slow process. The kinetics are, however, still well described by the mechanism outlined below, where the porphyrin is represented by N_4.

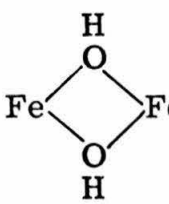
12) $$\text{py-FeN}_4\text{-py} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{py-FeN}_4 + \text{py}$$

13) $$2\ \text{py-FeN}_4 + O_2 \xrightarrow{k_3} \text{py-FeN}_4\text{-O}_2\text{-FeN}_4\text{-py}$$

We have represented the initial product as a peroxo-bridged dimer. An outer-sphere reaction producing two Fe(III) monomers is not entirely consistent with the kinetics. Also, free peroxide would almost certainly result from such a reaction mechanism , and there is some indirect evidence against H_2O_2 production, in as much as porphyrin ligands are generally susceptible to oxidation by H_2O_2, and no such ligand degradation is observed. (A probable

classic case of this is the report that Fe(II) tetrasulfatophthalocyanine forms a stable dimeric O_2 complex in aqueous solution.[194] One discovers on reading the original report that the evidence for an O_2 complex formulation was primarily that H_2O_2 did not seem to be produced. One other frequently referenced old report of a model iron-dioxygen complex is also appropriately mentioned at this point. On brief investigation three years ago, we found that the imidazole complex of (dimethylglyoximato)iron(II)[193] does indeed not give, on exposure to O_2, the yellow Fe(III) complex formed in the absence of imidazole. Instead, it gives a complex in which the dimethylglyoximato ligand has been oxidized. A likely cause of this behavior is that the imidazole complex is low-spin and kinetically inert.)

There are two possible decay routes of a μ-peroxo intermediate which do not produce peroxide. The first,

14) $FeO_2Fe^{4+} + 2Fe^{2+} + 2H^+ \rightarrow$  $+ 2Fe^{3+}$

is suggested by the isolation of μ-$(OH)_2$ dimers in the products of Cr^{2+} autoxidation, the bridging oxygens being derived from dioxygen.[209] It would, however, be extremely surprising if this reaction was very fast for iron, both faster than the preceding reactions, as required by the kinetics, and, particularly, faster than simple dissociation of the dimer (a competing reaction path which is unimportant for chromium(III) complexes, as for cobalt(III)

complexes). A compelling alternative to dissociation must be intrinsically fast, and must probably be unimolecular. A possibility which might fulfill these requirements is as follows:

15) $FeO_2Fe^{4+} \rightarrow 2\ FeO^{2+}$

16) $FeO^{2+} + Fe^{2+} \rightarrow FeOFe^{4+}$

O-O bond scission is not without precedent. The reactions of H_2O_2 with both Fe^{2+}[204] and Fe^{3+}[207, 213] involve such scission, and iron(IV) "ferrate", FeO^{2+}, is commonly invoked as an intermediate.[213] The reactions of several heme proteins with oxidants are thought to produce iron(IV) complexes.[208, 213] (Such assignments are, however, somewhat ambiguous.[204])

The reactions outlined above have direct analogies in the autoxidation chemistry of d^3 V(II). Reaction of V^{2+} with either O_2 or H_2O_2[211] gives vanadyl, VO^{2+}, directly, and VO^{2+} further reacts with V^{2+} to give a V(III) "hydrolytic dimer", VOV^{4+}, which decays slowly to V^{3+}.

It is, of course, true that VO^{2+} is a very stable chemical species, while FeO^{2+} is most definitely not. Furthermore, the μ-peroxo complexes discussed in chapter 4 showed no tendencies at all toward O-O bond scission. These problems are linked, however. Low-spin d^6 is a very stable configuration, and the chemistry of cobalt is largely a demonstration of that stability. On the other hand, high-spin d^5 Fe(III) (or even low-spin d^5) has no special stability associated with it. The point we are trying to establish is that reactions of Fe(II) with powerful (and potentially

2-electron) oxidants such as O_2 could easily involve Fe(IV) intermediates, and that a case (admittedly based on very flimsy evidence) can be made for such transients, the case becoming stronger when the hypothetical Fe(IV) intermediates would have strongly electron-donating ligands such as oxide.

We can now finally return to the pathways first-order in $[Fe^{2+}]$ observed in Fe(II) autoxidation. A remarkable variety of mechanisms have been proposed to account for the $[OH^-]^2$ dependence in equation 10), one of the most recent[202] invoking the hitherto unknown reagent O_2OH^- as a reactant. With at least an equal chance of being correct, we could suggest a rate-determining step of:

17) $$Fe(OH)_2 + O_2 \rightarrow FeO(O_2) + H_2O$$

That complexed hydroxides are important is suggested by the well-known sensitivity of ferrous hydroxide to air oxidation. In this formulation, the function of the hydroxo ligands is to stabilize an Fe(IV) intermediate. The acceleration of first-order pathways by ligands such as chloride could have a similar explanation. The intermediate itself, $FeO(O_2)$, is stabilized by two strongly electron-donating groups, and bears a notable similarity to the peroxide complexes of metal ions in high oxidation states discussed in chapter 5. It could undergo fast further reactions either dissociatively or by reactions with an additional Fe(II), most likely via oxo-bridging.

The kinetics of Fe(II) autoxidation certainly give no direct evidence of superoxide release, and one can at least mentally unify the kinetics by viewing them as proceeding in all cases from a relatively inert symmetrically bound peroxide-Fe(IV) intermediate which reacts irreversibly with Fe(II) to produce products, the rate of the reaction being a function of available bridging groups. We thus suggest that $d^6 \rightarrow d^4$ oxidative addition may be a valid description of the reaction of Fe^{2+} with O_2. The lack of examples of such oxidative addition may simply reflect the fact that most d^6 complexes are low-spin, and both kinetically inert and coordinatively unsaturated. (This is especially true for the second and third row metals ruthenium and osmium, for which the M(IV) state is rather stable.)

Realistically speaking, the arguments outlined here at most establish that Fe(IV) may be a relevant oxidation state in the consideration of iron-dioxygen complexes. We hoped to accomplish nothing more than this. We will now begin discussion of oxymetalloproteins.

Hemerythrin

Hemerythrin is a non-heme iron protein which performs an oxygen-carrying function in many organisms in invertebrate phyla. The protein from the sipunculid worm Goldfingia gouldii, upon which nearly all published work has been done, has a molecular weight of about 107,000 and consists of eight subunits, each of which contains two iron atoms and can bind a single dioxygen molecule.[215] Full

interpretations of the electronic structure of the oxygenated protein have been published,[216,217] and we will simply summarize conclusions and a few relevant data.

The electronic spectra and temperature-dependent magnetic susceptibilities of oxyhemerythrin and methemerythrin establish them to be extremely similar. Further, comparisons to model oxo-bridged iron dimers[219] show that the common unit is very probably an oxo-bridged iron(III) dimer. Oxyhemerythrin has an intense (ϵ = 1200/Fe) band at ~ 500 nm (which gives the oxy-protein its red-purple color). This band is readily assigned as a peroxide to Fe(III) charge transfer transition, completely analogous to the band at 515 nm of the ferric EDTA-peroxide complex discussed in chapter 4. The spectra of a variety of complexes of methemerythrin with complexing anions such as azide and thiocyanate have been published[218] (notably, these complexes form in the ratio of the two irons per anion) and the energies of the charge-transfer bands observed for these complexes make the comparison quite definitive.

The active site of the oxygenated protein can thus be described as an oxo-bridged iron(III) dimer with a peroxide ligand coordinated (end-on) to one of the irons. Because of the good agreement in magnetic properties of the oxy- and met- proteins, and also because of the charge-transfer band correlation, the peroxide is very probably not bridging. (Also, Mössbauer data show the irons to be non-equivalent.)[220]

A remaining unanswered question is why oxyhemerythrin does not release hydrogen peroxide, which is, of course, largely a question of the detailed protein structure around the site, of which almost nothing is known. Given the simple site we have described, there is nothing inherent in its electronic structure which should prevent dissociation. Furthermore, it is hard to understand how the protein could allow O_2 to enter and leave without also allowing peroxide to leave.

Two effects could possibly be operative. First, the protein could engage the bound peroxide in highly specific hydrogen-bonding interactions with protein groups. Dissociation of peroxide would require breaking these bonds as well as the bond to iron(III). Reductive elimination of O_2 would automatically turn off the hydrogen-bonding because of the reduced electron density on the O_2 unit. The low acidity of O_2H^- as well as complexed O_2H^- would enhance such interactions. (Oxyhemerythrin cannot be made from methemerythrin plus hydrogen peroxide,[221] which is probably related to the high pKa of H_2O_2, and the unavailability of O_2H^- or O_2^{2-} in aqueous solution at physiological pH's. The same factors which make peroxide a poor entering group might make it a poor leaving group in a properly constructed site.)

Secondly, a specific stereochemistry of the ligands other than oxide and peroxide bound to the irons could increase the reduction potential of the Fe(III)'s in the dioxygen adduct. Such an arrangement is suggested by the fact that the site must happily

coexist with two Fe(II)'s in deoxyhemerythrin. An "unusual" site is perhaps suggested by the energies and intensities of the observed ligand field bands for hemerythrin derivatives, which are both rather high. One or more of the Fe(III)'s being four- or five-coordinate would account for both effects. The experimental evidence is ambiguous, however. There may be a weak ligand field band at lower energy which has remained unobserved because of the tailing of higher energy bands.

The principal features of the electronic structure of the dioxygen-iron complex seem, however, unambigously clear. Dioxygen adds to a coupled pair of ferrous ions to give an "oxidative addition" complex of peroxide with a coupled pair of ferric ions.

Hemocyanin

Hemocyanin is a copper protein, found in molluscan, arthropodan and related species, which binds one O_2 molecule for every two copper atoms. The molecular weight is extremely high, and aggregation behavior is very complicated.[225]

In figure VI-1, we show the electronic spectrum of Busycon caniculatum (snail) oxyhemocyanin at room temperature and 5°K. The samples were prepared simply by spreading the centrifuged (viscous) protein on quartz plates and allowing them to dry in air for a few hours. Redissolution of films in buffer yielded substantially undenatured protein. The spectral results are summarized in Table VI-1, as well as the electronic spectrum of the protein in solution, for comparison. (Solution spectra were actually of some-

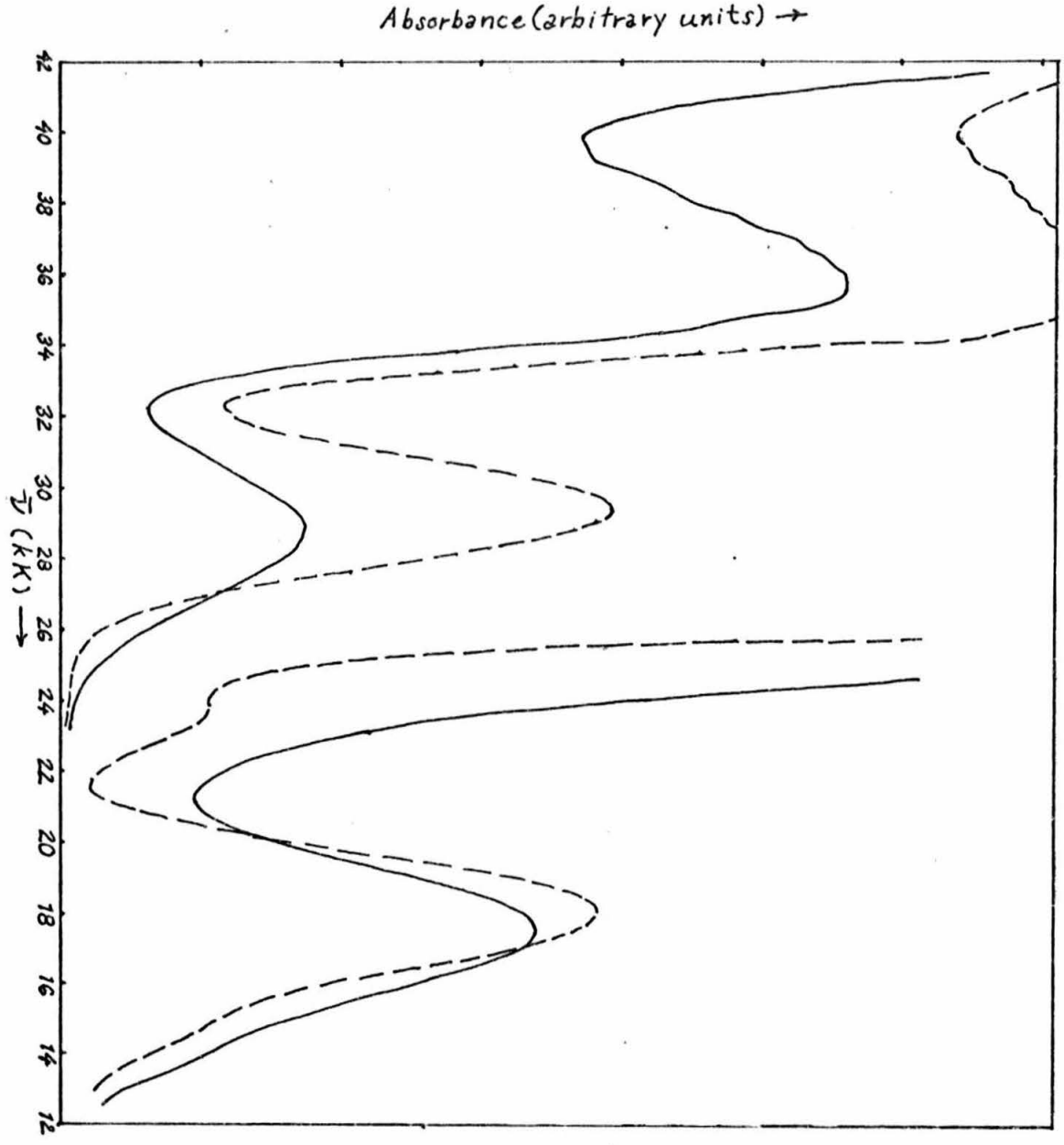


Figure VI-1. Electronic absorption spectra of Busycon caniculatum oxyhemocyanin, thin film on quartz plate, at R.T. (——) and 5 °K (----).

Table VI-1

Electronic Spectrum of Busycon caniculatum Hemocyanin

	Assignment	λ (nm)	ε/Cu or relative intensity
solution	ligand field	555	708
(phosphate buffer)	C.T., O_2^{2-} → Cu(II)	346	11,200
room temp.[a]	protein	279.5	39,300
film,	l.f.	570	1.00 (defined)
R.T.	C.T.	348	15.77
	protein	280	50.91
film,	l.f.	~690 (sh)	0.19
5°K	l.f.	555	1.00 (defined)
	l.f.	422	0.26
	C.T.	341	26.2
	protein	280	46.9

a) Total Cu concentration determined by atomic absorption spectroscopy.

what lower quality than film spectra at room temperature, because of scattering effects.)

At 5°K, three peaks which can be assigned to ligand field transitions are resolved. These peaks are also (barely) resolved in ethylene glycol-water glasses at 77°K, for both the snail protein and lobster protein. Van Holde[222] has reported similar results for octopus oxyhemocyanin at 77°K. The band pattern and energies are unmistakably those of a Cu(II) complex.[223] The intensities are somewhat enhanced over those of "normal" Cu(II) complexes (such as aqueous Cu^{2+}), but intensifications of this order are known for magnetically coupled Cu(II) dimers.[224] With no information on the ligands at the copper binding site, we cannot attempt assignment of the spectrum, but we note that for "relatively" weak distortions from octahedral symmetry, a case probably indicated as a reasonable approximation by the energies of the transitions, three d-d transitions are expected, $(xz, yz) \rightarrow x^2 - y^2$, $z^2 \rightarrow x^2 - y^2$, and $xy \rightarrow x^2 - y^2$, the first of these usually being more intense than the others.[223]

The intense transition at 346 nm ($\epsilon = 11,000$ in solution) is reasonably assigned to a peroxide-to-metal charge-transfer transition. It has no counterpart either in the spectra of copper(II) complexes[223] with non-reducing ligands (such as most amino acids) or in the spectra of other (non-oxygen carrying) copper proteins.[216] Unfortunately, there are no data in the literature on the energies of charge-transfer bands of $LnCuX^+$ species to

allow us to decide if the energy of the band is reasonable for the assignment. (This situation is related both to the kinetic lability of copper complexes, and to their tendency to react with ligands such as thiocyanate to produce Cu(I).)

Magnetic susceptibility studies, employing the ultra-sensitive magnetometer used to determine the magnetic susceptibility of oxyhemerythrin,[217] are in progress, but results have not been obtained at the time of writing. We thus do not have any measure of the order of magnitude of the magnetic coupling of the Cu(II)'s in the dimeric unit. (Or, much more importantly, complete assurance that the unit can be described as a Cu(II) dimer. The protein does not display an e.s.r. signal.[225])

The absence of either a charge-transfer correlation or magnetic susceptibility results prohibits us from making any conclusions as to the nature of the binding of the peroxide to the coupled Cu(II) dimer. The known preference of Cu(I) for low coordination numbers (2-4) leads us to believe that a natural mechanism for the oxygenation reaction would involve the dioxygen bridging the two coppers, simultaneously increasing both the oxidation state and coordination number of each copper by a single unit. Methemocyanin is not an easily obtained species, and may not be stable at all, which seems consistent with a low coordination number in the protein site. This would also enhance reversibility of the reaction, as dissociation of peroxide would then have a high activation energy.

At this point we can state that the active site in oxyhemocyanin is most probable well described as a peroxide ligand bound to a Cu(II) dimer, and oxygenation, just as in hemerythrin, can be described as two-electron oxidative addition to a coupled two-metal-ion site.

Hemoglobin

Hemoglobin is the most widely known and best-investigated dioxygen-carrying protein, most obviously because it is the human oxygen-carrying protein. Briefly, it is a protein of molecular weight 64,450 found in red blood cells, and has four dioxygen-binding sites per molecule. The dioxygen storage protein myoglobin, found in red muscle cells, has only one site, but is otherwise extremely similar, being approximately a one-quarter hemoglobin molecule. Detailed X-ray structures have been done for both proteins,[1] and the environment of the binding site elucidated. The most distinctive features of the site are the binding of ferrous iron by a protoporphyrin IX group, and the specific locations of two imidazole groups of histidine amino acid residues, the <u>proximal</u> imidazole, which is directly bound to the iron, <u>trans</u>- to the dioxygen binding site, and the <u>distal</u> imidazole, which is not directly bound, but is very near, in a pocket formed by the protein around the binding site.

A single dioxygen molecule is reversibly bound by each iron(II) porphyrin moiety in the proteins. Despite the (relatively speaking) enormous amount of information which we have on oxyhemoglobin, a tremendous controversy has existed and continues to exist over

the electronic structure (and even the geometric structure, since the O_2 unit has not been directly detected in the X-ray structural work) of the dioxygen adduct. (We may mention ahead of time that our present discussion will not resolve this controversy.)

There have been, traditionally, three models of O_2 binding. The classic Pauling model[226] supposed an "end-on" bound neutral O_2, the iron being low-spin d^6. Griffith[227] suggested a π-bound (symmetrically bound) neutral O_2 in 1956. Weiss,[228] in 1964, suggested an end-on bound spin-coupled superoxide-Fe(III) complex. An additional (non-classical) model was first suggested by Gray[216] in 1971, and involves coordination of peroxide to Fe(IV).

All of these models are designed, basically, to explain a single experimental result, the 1936 measurement of Pauling and Coryell[226] that showed the heme unit in oxyhemoglobin to be diamagnetic. Electronic spectroscopy is of little use for hemoglobin. The visible spectra of porphyrin derivatives are dominated by intense intra-ligand transitions, with weaker bands usually assigned[229,230] as porphyrin-to-metal transitions appearing in the near-infrared. A "distinctive" band of oxyhemoglobin does appear, at 915 nm ($\epsilon \simeq 200$). However, any attempt to assign this band is probably doomed to the fate best described recently by a prominent inorganic chemist,[231] "Even my mother didn't believe that assignment."

We will consider the various models in order. The models based on neutral dioxygen are attractive in that they easily account

for the diamagnetism of the complex, and maintain a stable low-spin d^6 configuration for the central metal-ion. However, we simply do not believe that a metal-ion as susceptible to oxidation as Fe(II) would maintain a ground state consistent with a half-filled O_2 π^* shell. This is essentially a prejudice, based on our experience with other dioxygen complexes.

The "superoxide" models are much in favor now, especially in view of the extensive work which has been done on cobalt complexes, for which this structure assuredly holds true. This model does have the point to recommend it that it invokes oxidative addition binding. However, we note that mention of the magic words, "antiferromagnetic coupling" is not enough to convince us of the viability of the model. For effective diamagnetism, the complex is required to be an O_2^- complex of low-spin Fe(III) with the two unpaired electrons spin-coupled. For the electrons to be coupled in two rather different molecular orbitals without having both electrons fall into one of the orbitals, the orbitals would have to be weakly-interacting and of nearly identical energies (considering spin-pairing energies.) The first requirement is barely possible as we showed in chapter 4 that the unpaired electron in Co(III) superoxide complexes resided in a largely non-bonding orbital. The second, however, requires such a delicate energy matching that we would have to regard it as a tremendous coincidence if it did prove to be the actual situation. If the electrons are coupled together in one of the two orbitals involved, even with some temperature dependence, the 0°K situation must necessarily

correspond to either a d^4 or d^6 central metal ion. (Increasing the interaction of the two presumably nearly-degenerate orbitals decreases the validity of this description, but it also decreases the applicability of the idea of antiferromagnetic coupling.) The idea of an antiferromagnetically coupled Fe(III)-O_2^- complex thus seems rather paradoxical to us. (An additional piece of information can be invoked. We found that O_2^- was spectrochemically similar to NCS^-, but the thiocyanate complex of metmyoglobin has considerable high-spin character.[212] If the dioxygen complex was partially high-spin, its full magnetism could not very easily be quenched at room temperature. Actually, it seems clear from our model that if electrons could thermally be in the metal $d\sigma^*$ orbitals, they would inevitably end up in the $O_2^-\pi^*$ hole.)

One fairly recent piece of evidence seems to support the superoxide model, a measurement of the iron X-ray fluorescence spectrum of oxyhemoglobin which supposedly indicates the iron to possess one unpaired electron.[210] As the method of measurement has no firm theoretical foundation as yet, and incidentally, shows metmyoglobin, which magnetic susceptibility measurements indicate to be high-spin,[212] to also have one unpaired electron, we will withhold judgment.

The final models under consideration is the peroxide-Fe(IV) model. Comments we have made as the viability of this model for iron autoxidation also apply here, and we can make no additional arguments. One question needs to be commented on, that of

diamagnetism. For an Fe(IV) complex to be diamagnetic simply requires a large splitting of the $d\pi$ metal orbitals, as could easily be accomplished by a symmetrically bound, or nearly symmetrically bound peroxide ligand. (We recall that such a ligand is a strong π-donor and would be interacting heavily with the $d\pi$ orbitals.)

Actually, in our formulation the distal imidazole would probably engage in hydrogen bonding interactions with one end of the peroxide, which might tend to stabilize it against dissociation as O_2^{2-} in a manner similar to that discussed for hemerythrin. That carbon monoxide complexes of mutant hemoglobins have ν(CO)'s considerably shifted from those of normal hemoglobins[232] illustrates the extreme suitability of the distal imidazole for hydrogen-bonding interactions.

We can finally mention one experiment which is support for a symmetrically bound peroxide model (and thus consistent with Fe(IV)) in a negative sense. Careful measurements of the solution infrared spectrum of oxyhemoglobin have failed to locate an O-O stretch.[216] Comparison to the known intensities of O-O stretches for model Co(III)-O_2^- monomers shows that a band <u>should</u> have been observed for an analogous complex. On the other hand, the bands for symmetrically bound peroxide complexes are much weaker and might be below the resolution limits of the experiment.

We can summarize the state of affairs in the continuing problem of the electronic structure of oxyhemoglobin as follows.

All physical measurements which have been performed on the protein up to this point in time do not allow any unique assignment of the electronic structure of the binding site to be made. This is primarily a problem of the non-specificity of the available measurements. (Unfortunately, very specific measurements such as electronic spectroscopy have thus far given uninterpretable results.) Given this state of affairs, conclusions can only be based on inference from more easily investigated systems, and the arguments we have presented here are such arguments. Our conclusions are thus highly fallible. (A measure of that fallibility is their notable disagreement with those of many other extremely competent workers in the field.) We cannot feel extremely confident about them, but we nevertheless feel obliged to present them.

Conclusion

If the only purpose of this work presented in this thesis was to elucidate the electronic structure of oxymetalloproteins, then it cannot be said to have been very successful. We have indeed arrived at some insights into oxymetalloprotein electronic structure, but the range of the insights is quite limited, and the insights are in no case assuredly correct. Fortunately, we are not so restricted. The systematicities we have observed in the electronic structures of dioxygen complexes, and the more general investigations we have been forced to make of the systematic correlations of charge-transfer and ligand field transitions in transition metal complexes, fit naturally into the body of knowledge of transition metal chemistry.

It is really rather nice to know that dioxygen complexes are metal complexes which can be considered in the same terms as complexes of other, less exotic ligands, and not mysterious modules involving "non-innocent" ligands. And, returning to the proteins, we can always say that some insight is better than no insight.

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